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WADC TECHNICAL REPORT 55-324

**DEVELOPMENT OF CHEMICALLY RESISTANT,  
HIGH-TEMPERATURE PROTECTIVE FABRIC**

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A. S. KIDWELL

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**JANUARY 1956**

**MATERIALS LABORATORY  
CONTRACT No. AF 33(616)-2544  
PROJECT No. 6312  
TASK No. 6448**

**WRIGHT AIR DEVELOPMENT CENTER  
AIR RESEARCH AND DEVELOPMENT COMMAND  
UNITED STATES AIR FORCE  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

Approved for Release by NSA on 09-11-2013 pursuant to E.O. 13526

## FOREWORD

This report was prepared by The Connecticut Hard Rubber Company, New Haven, Connecticut, under USAF Contract No. AF 33(616)-2544. The contract was initiated under Project No. 6312, "Ground Crew Protective Clothing," Task No. 64498, "Rocket Propellant Protection," formerly RDO No. 666-350, "Protective Clothing Against Special Hazards," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. C. W. Long acting as project engineer.

The period covered by this report is from 1 June 1954 to 31 July 1955.

## ABSTRACT

A coated fabric comprising a thin coating of aluminum-pigmented polychlorotrifluoroethylene on glass fabric backed with a low-density silicone rubber sponge, and having an overall thickness of 0.070 inch, was developed for use in protective clothing for personnel in danger of being exposed briefly to a chemical fire at temperatures up to 1000°F. The fabric shows excellent resistance to fuming nitric acid and other oxidizers and fuels, is flexible and useful over a temperature range of -80°F to +390°F.

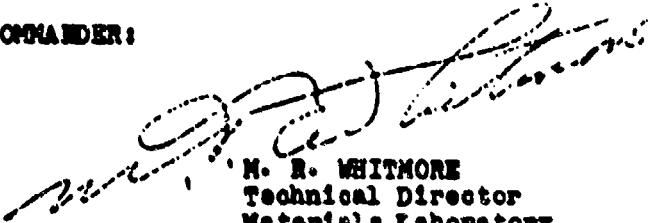
This fabric construction showed a temperature rise on the inside surface of less than 100°F after direct exposure to a flame caused by mixing white fuming nitric acid and monoethyl-aniline. Peak-flame temperatures averaging about 1600°F three seconds after mixing the reactants were measured with thermocouples. The fabric was non-porous to 1000°F steam, and was not penetrated by reaction products of the ethyl aniline-fuming nitric acid combustion.

Polyethylene and polyethylene-Vistanex blends were cured with peroxide and were resistant to temperatures of 250°F. They also showed improved resistance to penetration by white fuming nitric acid.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE  
Technical Director  
Materials Laboratory  
Directorate of Research

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## INTRODUCTION

The object of this contract was to develop a material suitable for the fabrication of protective clothing for personnel who might be exposed briefly to a chemical fire at temperatures up to 1000°F. The material was to be resistant to white fuming nitric acid, monoethylaniline and hydrazine (94 percent). It was to be flexible throughout the temperature range of -67°F to 157°F.

In the handling of the special fuels which are used in guided missiles, personnel are liable to be exposed to fuming nitric acid and other oxidizing agents. Under Contract No. AF 33(616)-155, The Connecticut Hard Rubber Company developed a chemically resistant coated fabric suitable for the fabrication of protective clothing to be used under normal temperature conditions. This clothing, however, would not protect the wearer should fuels accidentally ignite. On the other hand, there are a number of rescue suits presently in use which will withstand reasonable exposure to 1000°F. They, however, are permeable to fuming nitric acid and to the toxic reaction products, such as the superheated vapors, found when rocket fuels are ignited. Also, these rescue suits are generally quite heavy and awkward, and would be very uncomfortable as protective clothing for daily work use.

At a meeting held at Wright Air Development Center on June 2, 1954, it was decided that the material developed under this contract would be used in the fabrication of a lightweight escape suit rather than a rescue suit.

Although no great pressure is exerted when rocket fuels are ignited in an unconfined space, an individual in the immediate area would be spattered with unreacted fuming nitric acid or fuel. He would also be exposed to flames and temperatures of about 1000°F. At this temperature, any atmospheric moisture, reactants, or reaction products would be turned to superheated vapors. With these factors in mind, a fabric was designed consisting of a thin layer of silicone rubber sponge on glass fabric coated with a heat-reflective acid-resistant barrier as a protection against possible splashing with white fuming nitric acid in daily use. A protective suit made from a fabric of this kind would be relatively light in weight, flexible, and reasonably comfortable to the wearer.

As described in this report, a number of samples were

1. Footnotes refer to references in Bibliography.

prepared by varying the component layers. These samples and various samples of commercial fabrics were subjected to radiant heat and superheated steam of 1000°f. Acid-resistant coating materials were compared by the H-Cell permeability test. The best constructions were exposed to a flame produced by mixing white fuming nitric acid with monoethylaniline, and the heat penetration and effect on the fabric surface were noted.

## ASSIGNMENT

Contract No. AF 33(616)-2544, effective 1 June 1954, stipulates research and development of a chemically resistant fabric which will provide protection against proximity to flame at 1000°F.

### Articles or Services

A. Develop a fabric or fabric combination capable of protecting a man splashed with white fuming nitric acid and concurrently exposed to a heat of 1000°F. The fabric shall also possess chemical resistance to monoethylaniline and hydrazine (94%).

B. The fabric or fabric combination must have the following target properties:

1. Suitability for fabrication by known techniques of the clothing industry
2. Good seam efficiency and stability
3. Adequate abrasion- and flex-resistance
4. Shall not give off fumes upon application of 1000°F heat, which would injure personnel
5. Good flexibility when tested according to flexibility test in USAF Specification MIL-F-4143, except high temperature shall be 157°F instead of 170°F and the low temperature shall be -67°F

C. Furnish 100 yards of fabric, not less than 36 inches wide, on completion of contract.

D. Prepare and furnish 20 copies of each of three quarterly progress reports, and 20 copies of a final summary report.

## EXPERIMENTAL PART

### Experiment 1: Comparative Heat-Stability of Selected Silicone Rubber Compounds

**Object:** To obtain data on the heat-stability of various silicone rubber compounds by aging cured slabs at 700°F.

**Results:** As a result of aging tests on seven silicone rubber compounds, two were selected for the best retention of elongation and tensile strength for extreme high-temperature work. The two compounds, 207-5 and 217, survived eight hours' aging at 700°F, the former showing slightly better physical characteristics after aging. Samples of Compound 207-5, after eight hours' aging, showed an average tensile strength of almost 600 psi with 25 percent elongation, while Compound 207-1, after only four hours' aging, displayed a tensile strength of 490 psi and only 10 percent elongation. Samples of Compound 207-1 were too brittle to be tested after eight hours of aging. Various blends of Compound 207-1 and Compound 207-5 were also aged, improvement being noted as the percentage of Compound 207-5 in the blend was increased.

**Procedure:** Several 6 x 6 x 0.075 inch test slabs were prepared from each compound and were subjected to a press cure of 15 minutes at 250°F, followed by an oven cure of 24 hours at 480°F. The samples were cut into 1 x 6 inch strips which were aged in a circulating air-oven at 700°F. After the aging, standard dumbbells were die-cut from the strips, and physical properties were determined.

**Data:** See Table 1

**Discussion:** It is felt that Compound 207-5 showed the aging properties most desired for a high-temperature-resistant sponge-fabric compound, where retention of softness and elongation are of prime importance.

Compound 208 was included here as a specific flame-resistant compound.

TABLE 1

HIGH-TEMPERATURE (700°F) AGING OF SILICONE RUBBER,  
SUITABLE FOR USE AS SPONGE IN ACID- AND FLAME-RESISTANT FABRIC<sup>1</sup>

Compound No.		Modulus		Tensile, Psi	Elong., %	Hardness, A Duro.
		100%	200%			
207-1	Control <sup>2</sup>	380	625	625	200	75
	4 Hrs @ 700°F			490	10	100+
	8 Hrs "			Too Brittle		
	8 Hrs "			Too Brittle		
207-2 <sup>3</sup>	Control <sup>2</sup>	370	730	730	200	68
	4 Hrs @ 700°F			630	25	96
	8 Hrs "			Too Brittle		
	8 Hrs "			Too Brittle		
207-3 <sup>4</sup>	Control <sup>2</sup>	340	655	755	225	63
	4 Hrs @ 700°F			460	40	88
	8 Hrs "			600	10	99
	8 Hrs "			710	15	99
207-4 <sup>5</sup>	Control <sup>2</sup>	345	625	740	250	58
	4 Hrs @ 700°F			440	50	80
	8 Hrs "			655	25	94
	8 Hrs "			640	15	94
207-5	Control <sup>2</sup>	310	645	910	300	55
	4 Hrs @ 700°F			585	40	84
	8 Hrs "			630	25	93
	8 Hrs "			545	25	92
208	Control <sup>2</sup>			515	75	58
	4 Hrs @ 700°F			730	15	98
	8 Hrs "			575	10	100+
	8 Hrs "			Too Brittle		100+
217	Control <sup>2</sup>	280	675	675	250	50
	4 Hrs @ 700°F			465	25	87
	8 Hrs "			670	15	94
	8 Hrs "			700	15	95

## Notes:

1. Type "C" jaws used on Scott Tester with samples having less than 25 percent elongation; otherwise standard Z clamps used.
2. All samples press-cured 15 minutes at 250°F and oven-cured 24 hours at 480°F before aging.
3. Blend of 75 percent Compound 207-1, 25 percent Compound 207-5.
4. Blend of 50 percent Compound 207-1, 50 percent Compound 207-5.
5. Blend of 25 percent Compound 207-1, 75 percent Compound 207-5.

## Experiment 2: Development of Sponge-Fabric

**Object:** To develop a sponge compound to meet the specific requirements for a high-temperature-resistant, insulating sponge-fabric, i.e., minimum density, softness, flexibility, and stability at high temperature.

**Results:** With the use of the soft, high-temperature-resistant compound selected from the previous experiment, Compound 207-5, a flexible sponge-glass fabric combination of very low density was developed, suitable for continuous blowing and curing in standard production equipment. The specific gravity of the No. 116 glass fabric-sponge combination was 0.22 at a thickness of 3/16 inch, 0.26 at 1/8 inch, and 0.35 at 1/16 inch. The thickness after blowing and curing was found to be quite reproducible ( $\pm 5$  percent, or less), and curves relating over-all final thickness and specific gravity with over-all initial thickness were made (Figures 1 and 2) to facilitate production of sponge-fabric of any desired thickness and of minimum density. The selected silicone rubber sponge compound was designated as Compound No. 233.

**Procedure:** A total of fifty-nine sponge-fabric samples were fabricated by the following general procedure. The base silicone rubber compound was prepared by blending the gum and filler on a small laboratory rubber mill. To this were added varying amounts of blowing agent and curing catalyst. Five different blowing agents and three different curing catalysts, covering a wide range of activating temperature, were tested over wide variations in concentration. The blowing agent and catalyst were carefully blended into the rubber stock on a cold mill, and the stock was refined to produce uniform and reproducible blowing. The sponge compounds were then calendered onto No. 116 glass fabric to the desired initial thickness. Most of the samples were blown from an initial total thickness of 0.035 inch; some were varied in initial thickness from 0.020 inch to 0.040 inch. A flat metal clamp was attached to each end of each strip, and the strips were suspended in a circulation-air oven to be blown and cured. All samples were blown and cured within two hours after preparation of the compound to minimize any degradation of blowing agent or catalyst. The oven blowing temperature was varied over the range 300°-480°F. All samples were heated at the blowing temperature for 30 minutes, and were then cured for one hour at 480°F.

**Data:** See Figures 1 and 2

**Discussion:** See the main Discussion Section of this report.

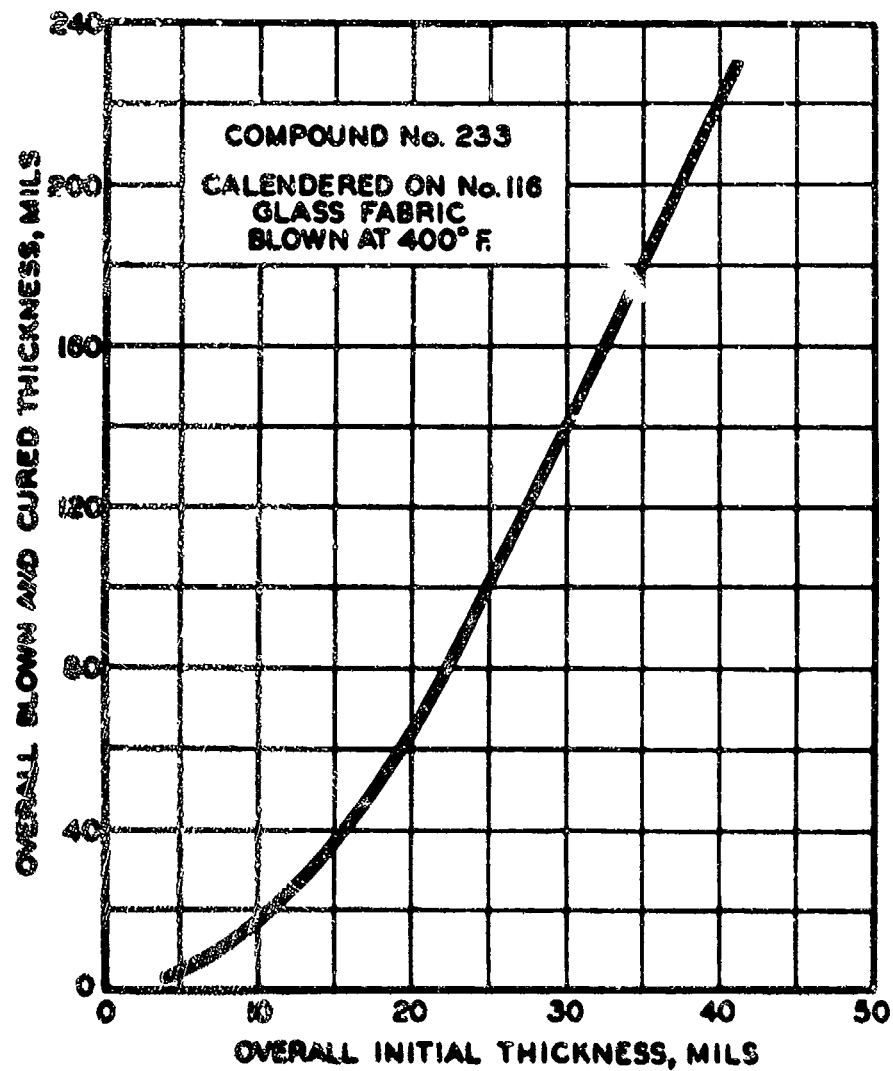


FIG. 1 FINAL SPONGE-FABRIC THICKNESS  
AND INITIAL THICKNESS

### Experiment 3: Preparation of Sponge-Fabric in Laboratory Tower

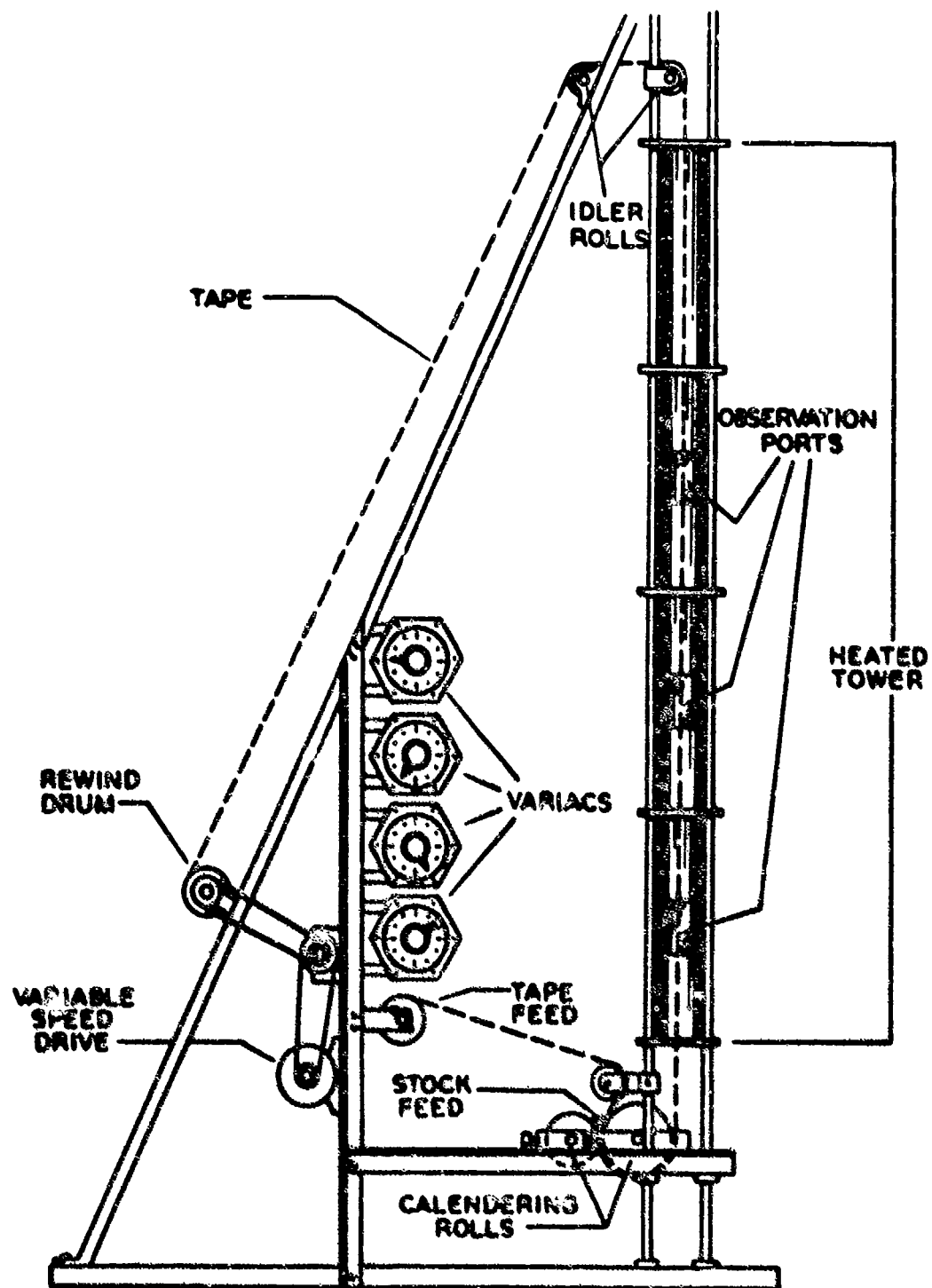
**Object:** To prepare sponge-fabric in continuous lengths, using a laboratory tower to blow and cure the sponge.

**Results:** Continuous lengths of glass fabric coated on one side with a soft, low-density silicone rubber sponge were fabricated with the use of a four-zone electrically heated pilot-scale tower. Over-all blown thicknesses were varied from 0.074 inch to 0.035 inch, with total weights of 1.21 and 0.86 pound per square yard, respectively. The glass fabric tape used was somewhat heavier than the No. 116 glass fabric used in the previous experiment. The sponge, alone, showed specific gravities of 0.29 and 0.42, respectively. Up to 25 parts of carbon tetrachloride added to small portions of the compound as a softener showed no detrimental effect on the sponge product. Both the sponge compound and the continuous method were considered quite satisfactory.

**Procedure:** Figure 3 is a drawing of the laboratory vertical tower into which glass fabric tape was fed. The tape passed through two calender rolls at the base of the tower, then passed up through the four electrically heated and individually controlled zones, each being two feet in length, then out of the top of the tower and to a take-up reel. The take-up reel and the larger calender roll were driven. The tape passed through the four zones, a distance of eight feet, at a rate of twelve inch per minute, resulting in a total heating time of eight minutes.

The silicone rubber sponge compound, No. 233, developed in the previous experiment, was prepared on a laboratory rubber mill just prior to use. The compound was removed from the mill in a convenient thickness and was fed into the tower calender rolls to coat the glass fabric tape. Up to 25 parts of carbon tetrachloride was added to small portions of the stock as a softener, reducing the calender load and stress on the tape.

**Data:** Glass fabric tape, two inches by 0.005 inch, weighing 4.2 ounces per square yard, was used. The tape speed was maintained at twelve inches per minute. The optimum tower temperature ranged gradually from about 350°F in the bottom zone to about 450°F in the top zone. Samples cut from the tapes are described in Table 2.



**FIG. 3 PILOT SCALE COATING TOWER**

TABLE 2

SPONGE-TAPE DATA

<u>Sample No.</u>	<u>Total Blown Thickness, Inch</u>	<u>Weight lbs/sq yd</u>	<u>Specific Gravity</u>	
			<u>Total</u>	<u>Sponge, Alone</u>
112	0.074	1.21	0.35	0.29
109	0.065	1.15	0.38	0.31
111	0.057	1.03	0.39	0.31
110	0.035	0.86	0.52	0.42

---

Discussion: See the main Discussion Section of this report

Experiment 4: Dispersion of a Silicone Sponge Compound  
in Toluene and Carbon Tetrachloride

**Object:** To prepare soft paste-dispersions of a silicone rubber sponge compound, using either toluene or carbon tetrachloride as a dispersant. To prepare sponge fabrics and to determine the effect of those solvents on curing and blowing, as compared with results obtained with undispersed compound (Experiment 2).

**Results:** The silicone rubber sponge compound can be dispersed in either of the above solvents. However, the specific gravities of the sponge samples made by dispersion-coating were considerably higher than those obtained with undispersed compound i.e., the ability of the compound to sponge was seriously decreased by the presence of the solvents. Toluene was found to be more deleterious than carbon tetrachloride (see Table 3).

**Procedure:** The silicone rubber sponge compound, No. 233, selected in Experiment 2, was prepared on a small, laboratory rubber mill, and was then dispersed in toluene or carbon tetrachloride with the use of a small Hobart electric mixer. Dispersions with solid contents varying from 23 to 52 percent were made in this manner. Dispersions having high solid contents were prepared on the mill. The dispersions were spread on No. 116 glass cloth by means of Knowlton knife-coater in the case of the less viscous mixtures. The stiffer mixtures were applied by a three-roll, laboratory calender, as noted in Table 3. After a drying period of one hour at room temperature, the samples were suspended and cured in an air-circulating oven for 30 minutes at 400°F. The specific gravity and weight per square yard of each sample were then measured and recorded.

**Data:** Data may be found in Table 3.

TABLE 3

## EFFECT OF DISPENSING A SILICONE RUBBER POWDER COMPOUND IN TOLUENE OR CARBON TETRACHLORIDE

Sample No.	Solid Content %	Solvent	Mixing Method	Over-all Coating Thickness, Inch	Over-all Thickness, Inch Blown	Sp O <sup>2</sup> Weight, lb/sq yd	Remarks Processability	Remarks Product	
125	27	Toluene	Mixer Knowlton	.010 <sup>a</sup>	.017 <sup>a</sup>	.85	.64	Coating penetrated cloth	Good Appearance
126	30	"	Mixer Knowlton	.008 <sup>a</sup>	.012 <sup>a</sup>	1.40	.59	Coating penetrated cloth	" "
127	39	"	Mixer Knowlton	.013 <sup>a</sup>	.021 <sup>a</sup>	.56	.73	Good	" "
128	52	"	Mixer Knowlton	.015 <sup>a</sup>	.025 <sup>a</sup>	.61	.90	Too stiff for Knowlton coater face slightly rough	Pair appearance; surface slightly rough
129	74	"	Mill Calendar	.010 <sup>a</sup>	.020 <sup>a</sup>	.673	.706	Good	Good Appearance
130	23	CCl <sub>4</sub>	Mixer Knowlton	.016 <sup>a</sup>	.026 <sup>a</sup>	.58	.81	Good	" "
131	35	CCl <sub>4</sub>	Mixer Knowlton	.012 <sup>a</sup>	.020 <sup>a</sup>	.57	.59	Good; slightly stiff	Surface slightly rough
132	68	"	Mill Calendar	.012 <sup>a</sup>	.030 <sup>a</sup>	.50	.88	Good	Good Appearance
133	88	"	Mill Calendar	.016 <sup>a</sup>	.037 <sup>a</sup>	.47	.945	Very Good	" "
107	100	-	Mill Calendar	.020 <sup>a</sup>	.065 <sup>a</sup>	.30	1.05	" "	" "
97	100	-	Mill Calendar	.035 <sup>a</sup>	.181 <sup>a</sup>	.206	1.9	" "	" "
113	100	-	Mill Calendar	.052 <sup>a</sup>	.250	.213	2.66	" "	" "

1. Unblown thickness of fabric (0.004<sup>a</sup>) and coating, after removal of solvent

2. Specific gravity of sponge alone (excluding fabric)

3. Over-all weight of the product, fabric (0.20 lb/sq yd) and a sponge

## Experiment 5: Application of Acid-Resistant Coatings

Object: To determine the best methods for applying various acid-resistant barrier materials onto the face of heat-resistant fabrics. (The question of adhesion is covered in Experiment 6).

Results: Several satisfactory coating techniques were developed, and samples were prepared for H-cell tests. Polyfluoron, Kel-F Elastomer, and a polyethylene-Vistanex blend were used as acid-resistant coatings.

### Procedure:

#### 1. Spray Coating

##### a. Polyfluoron (polychlorotrifluoroethylene)

Two 6 x 6 inch samples of Vacal-fabric (vacuum-deposited aluminum on No. 116 glass fabric) were fastened to an aluminum sheet and stretched tight. A Polyfluoron dispersion, diluted with Dispersant "A" to about 20 percent solids, was sprayed on the Vacal-fabric to a wet thickness of about 0.002 inch, and the samples were immediately placed in an oven at 480°F for 20 minutes. The samples were then removed from the oven, and one of them was quenched in water. This procedure was repeated twice, the one sample being quenched after fusion of each coating. A good film resulted, approximately two mils thick, but a brownish color was evident in the coating. Several pairs of samples were run to check this phenomenon, but the brown color persisted.

In order to eliminate this coloration, the Vacal-fabric was pretreated at 600°F for one hour to remove any volatile material. When the pretreated fabric was spray-coated in the manner described above, a colorless, transparent coating (0.002 inch) resulted. A drop of fuming nitric acid placed on the surface did not appear to penetrate or discolor the aluminum beneath.

The above Polyfluoron dispersion was modified by the addition of 10 parts by weight of aluminum powder per one hundred parts of resin solids. This material was spray-coated onto No. 116 glass fabric, fused, and quenched as above. Two coats were followed by one coat of clear Polyfluoron to yield a finished coating, 0.002 inch in thickness.

## b. Kel-F Elastomer

Two 6 x 6 inch samples of Vacal-fabric were fastened to an aluminum sheet and spray-coated with a 5 percent solution of Kel-F Elastomer gum in a mixture of methyl isobutyl ketone and toluene (50:50), to which had been added 3 parts of benzoyl peroxide. Eight spray passes were applied, four in each direction. The coating was dried and then baked at 300°F for 30 minutes. Due to the fact that the Vacal-fabric was not heat-treated, the brown color was again in evidence, but otherwise the coating appeared to be very good. On repeating the above procedure using heat-treated Vacal-fabric, colorless, transparent coatings, about 0.002 inch thick, were obtained. A drop of fuming nitric acid did not appear to penetrate the coating nor was the aluminum beneath discolored.

## c. Polyethylene-Vistanex (40:60 blend)

Attempts were made to spray-coat Vacal-fabric with a 5 percent solution of the polyethylene-Vistanex blend in toluene. Good films were not obtained, due to the viscosity of the solution. Further experimentation on this method was not considered practical at that time.

## 2. Knife Coating

### a. Polyfluoron (polychlorotrifluoroethylene)

A holland cloth leader was stretched in the Knowlton Coater, and two 6 x 6 inch samples of heat-treated Vacal-fabric were taped flat to its surface. The knife was adjusted to just clear the samples, and the Polyfluoron dispersion (41 percent solids) was placed on the leader. The knife was then smoothly drawn over the samples to give an even coating. The knife was reset, and a pass was made in the opposite direction. Fusion was accomplished by baking at 480°F for 20 minutes. Samples were quenched after fusion. This procedure resulted in a fused coating having a thickness of about 0.0005 inch. Two more coats were applied in the same manner, a final coating having a thickness of about 0.0015 inch being obtained. A smooth, even coating resulted which was apparently impervious to fuming nitric acid (drop test). No brown discoloration was evident in any of the samples.

The above Polyfluoron dispersion (41 percent solids) was modified by the addition of 10 parts of aluminum powder per one hundred parts of resin solids. This mixture was knife-coated onto No. 116 glass fabric, fused, and quenched as

above. Two coats were followed by one coat of clear Poly-fluoron to result in a finished coating, 0.002 inch in thickness.

b. Kel-F Elastomer

Two 6 x 6 inch samples of Vacal-fabric were taped to the leader, and coatings were prepared in the manner described above, using a 10 percent solution of Kel-F Elastomer gum, to which 3 parts of benzoyl peroxide were added. The coating was allowed to air-dry to a tacky consistency before the samples were placed in an oven at 300°F for 30 minutes. A smooth, even coating, about 0.00025 inch thick, resulted. Two more coatings were applied in the same way, a final coating having a thickness of about 0.00125 inch being obtained. The coating was transparent and quite flexible.

Aluminum powder (10 parts per one hundred parts of polymer) was added to the Kel-F Elastomer solution above. This mixture was knife-coated onto No. 116 glass fabric in the same manner as above, and was dried and cured. Two coats were followed by one clear coating to produce a finished coating, 0.002 inch in thickness.

Knife-coatings were also made on No. 116 glass fabric using Kel-F Elastomer compounded as follows (designated Compound No. 89 by the M. W. Kellogg Company and recommended for acid-resistance):

Kel-F Elastomer	100	parts
Zinc Oxide	10	"
Dyphos	10	"
Benzoyl Peroxide	3	"

This compound was prepared on a standard rubber mill and was dispersed as 10 percent solids in a 50:50 mixture of methyl isobutyl ketone and toluene. Three coats were applied, as above, to produce a finished coating, 0.002 inch in thickness.

c. Polyethylene-Vistanex (40:60 blend)

No difficulty was encountered in the knife-coating of the polyethylene-Vistanex blend, provided the solution was applied hot (160-180°F). A 5 percent solution was used in this experiment. The hot solution was poured onto the leader, and the Vacal-fabric samples were knife-coated once in each direction. They were then allowed to air dry before being finally dried in an oven at 160°F for 15 minutes.

Three coats were applied in this way, and an excellent film, about 0.002 inch thick, resulted. A drop of fuming nitric acid did not appear to penetrate the film.

The above solution of polyethylene-Vistanex was pigmented with 10 parts of aluminum powder per one hundred parts of polymer, and knife-coated onto No. 116 glass fabric. Two coats were followed by one clear coating to produce a finished coating, 0.002 inch in thickness.

Discussion: See main Discussion Section of this report.

Experiment 6: Adhesion of Sponge and Acid-Resistant Coating to Glass Fabric

**Object:** To obtain satisfactory adhesion of a Polyfluoron coating and a silicone sponge rubber coating on opposite sides of glass fabric.

**Results:** Satisfactory adhesion of both the aluminum-pigmented Polyfluoron coating and the silicone rubber sponge on glass fabric was obtained by an initial spray application of a thin priming coat of Polyfluoron to one side of the glass fabric before calendering the silicone rubber compound on the opposite side. Application of the rubber compound as the first step, followed by spraying or knifing the Polyfluoron on the opposite side of the fabric resulted in poor adhesion of the Polyfluoron to the glass (and rubber) surface. Completion of the Polyfluoron coating (0.002 inch thick) on one side of the glass fabric before application of the rubber compound to the opposite side resulted in sufficient strike-through of the plastic to cause poor adhesion of the rubber coating to the fabric.

Standard glass fabric (as received) showed approximately the same results as heat-treated glass fabric (organic sizing removed).

**Materials:** No. 116 glass fabric

(a) As received

(b) Heat-treated (heated at elevated temperature to burn-off the organic sizing)

Polyfluoron dispersion, 10 parts aluminum powder per 100 parts resin solids added, diluted to 20 percent and 10 percent solids with Dispersant "A".

Dispersant "A" (a chlorinated hydrocarbon solvent)  
Silicone rubber sponge compound No. 233 (see Experiment 2)

**Procedure:** Polyfluoron dispersion (40 percent solids) was diluted to 20 percent or 10 percent solids by the addition of Dispersant "A", and was applied as a thin spray coating on glass fabric. The fabric samples were placed in an oven at 480°F for 20 minutes, then removed and quenched. Silicone rubber sponge compound No. 233 was applied by means of a three-roll calender to the opposite side of the cloth. The sponge-fabric was placed in an oven at 400°F, for 30 minutes,

to blow and cure the sponge. (As indicated in Table 4, the sponge compound was applied as the first coating on several of the samples.) Two heavier spray coatings of Polyfluoron were then applied to the fabric and fused, individually, to result in a final coating thickness of 0.006 inch.

Strips, 8 inches by 1 inch, were cut from the fabric samples, and the Polyfluoron coating was peeled off at a 180° angle on a Scott Tester to determine the strength of the bond between the Polyfluoron film and the glass fabric.

Data: See Table 4.

TABLE 4

ADHESION OF POLYFLUORON TO GLASS FABRIC

No. 116 Glass Fabric	Order of Application of Coatings				PF-Glass Adhesion lb/in Width
	1st	2nd	3rd	4th	
A.R. <sup>1</sup>	20% PF <sup>3</sup>	Sponge	20% PF	20% PF	1.50
H.T. <sup>2</sup>	"	"	"	"	1.50
A.R.	10% PF	"	"	"	1.25
H.T.	"	"	"	"	1.00
A.R.	Disp. A <sup>4</sup>	"	"	"	1.00
H.T.	"	"	"	"	0.50
A.R.	Sponge	10% PF	"	"	0.25
H.T.	"	"	"	"	0.75
A.F.	"	Disp. A	"	"	0.10
H.T.	"	"	"	"	0.10

1. As received No. 116 glass fabric
2. Heat-treated No. 116 glass fabric
3. Polyfluoron dispersion, to which 10 parts  
aluminum powder were added
4. Dispersant "A"

### Experiment 7: Peroxide Cure of Polyethylene and Polyethylene-Vistanex Blends

**Object:** To determine the curing effect of dicumyl peroxide in polyethylene and polyethylene-Vistanex blends, as evidenced by physical properties, softening point and elevated-temperature relaxation.

**Results:** The addition of four parts, or more, of dicumyl peroxide to polyethylene, followed by heating under pressure at 325°F, effected appreciable cross-linking of the polymer chains, as evidenced by the loss of characteristic flow properties of the polymer at 250°F. The addition of four parts of the peroxide to an 80:20 blend of polyethylene: Vistanex effected considerable improvement in the physical properties and again produced a cross-linked product which did not flow under load at 250°F. In a 60:40 blend of Polyethylene and Vistanex it appeared that the peroxide was effecting cross-linking only in the polyethylene. While the blend produced a cured material stable under load at 250°F, the Vistanex portion of the blend apparently was somewhat depolymerized resulting in a tacky surface, and reduced tensile strength, elongation, and hardness.

The physical properties of polyethylene were varied considerably by the addition of one to eight parts of dicumyl peroxide (Figure 4). One and two parts of the curing catalyst caused some softening and a large increase in ultimate elongation, together with a considerable increase in tensile strength. Elongation and tensile strength both reached a maximum with two to three parts of the catalyst and fell off rapidly with six and eight parts to values somewhat above those for the uncatalyzed control. The stress-strain curve (Figure 5) showed comparatively little change in shape, mainly extending in length with the high-elongation compounds.

A high-temperature relaxation test indicated best the effect of the peroxide cure of the polyethylene (Figure 6). The control sample became a soft fluid within a minute after being placed in an air-circulating oven at 250°F. One part of the peroxide decreased the flow slightly. The polymer containing two parts of catalyst elongated slowly, finally rupturing at an elongation of 87 percent after thirteen hours. Four and six parts of catalyst effected practically no elongation up to about twenty hours, when a gradual increase occurred. The polymer containing eight parts of catalyst showed no change in elongation after twenty-four hours at 250°F.

Softening points of the polyethylene compounds varied little or none with varying amounts of catalyst (Figure 7). This property, controlled mainly by the melting of the crystallites, was apparently unaffected by the cure.

Resistance of the polymers to penetration by white fuming nitric acid was increased significantly by the peroxide cure (Table 7 and Figure 8). The resistance of the polyethylene-Vistanex blends was considerably better than that of the polyethylene above, which agrees with results found earlier in this laboratory under another contract (1) .

**Procedure:** Compounds comprising one hundred parts of polyethylene (Alathon No. 1) and one to eight parts of dicumyl peroxide were prepared by mixing the softened polymer with the peroxide on a standard laboratory rubber mill, the rolls being maintained at a temperature of 180°F. The resulting blends were compression-molded into 6 x 6 x 0.063 inch sheets in a hydraulic press at 325°F for thirty minutes under 500 psi pressure, followed by an oven cure of one hour at 300°F. Blends of polyethylene with Vistanex B-80 were prepared in a similar manner.

The physical properties were determined on a Scott Tester, using one-quarter-inch dumbbell samples cut from the molded sheets.

For the relaxation test, duplicate strips, 2 3/4 x 1/2 inch, were cut from the molded sheets, and two parallel lines, one inch apart, were marked at the center of each strip. A clamp provided with rubber inserts was secured to each end of the strips. A suitable weight to provide the desired loading (10 lbs/sq in.) was attached to one clamp on each strip, and the other clamp was used to suspend the strips in an air-circulating oven at 250°F. After removal of the strips from the oven, the clamps were detached and the strips were allowed to rest at room temperature for one hour, after which the tension was measured and expressed as percentage of the maximum elongation which had been reached at 250°F.

The softening points were measured by a procedure closely approximating ASTM-D-648-45T. Test strips, 2 3/4 x 1/2 x 1/16 inch, were placed on parallel supports, two inches apart. A load of 21.5 grams was applied to the center of the strips,

midway between the parallel supports, two inches apart. The assembly was immersed in glycerine, and the temperature was slowly raised to 180°F. The bending of the strip by the load, indicated by the downward deflection of the load, was noted as the temperature was increased.

The acid-penetration tests were run in the H-Cell with white fuming nitric acid (see Experiment 10 for a description of the H-Cell and procedure). The polyethylene and polyethylene-Vistanex blends were compression-molded into 6 x 6 x 0.010 inch sheets, and press-cured and oven-cured as described above on the thicker sheets. The 0.010 inch sheets were placed in the H-Cell as diaphragms, as described in Experiment 10.

Data: See Tables 5, 6, and ~ and Figures 4 to 8.

Discussion: See the main Discussion Section of this report.

TABLE 5

PHYSICAL PROPERTIES OF POLYETHYLENE COMPOUNDS

Press-Cured 30 Minutes at 325°F, Oven-Cured 1 Hour at 300°F

Curing Agent <sup>1</sup> , Phr <sup>2</sup>	Thickness, Inch	Modulus, psi			Tensile, psi	Elongation, %	Hardness Shore "D"
		100%	200%	400%			
0	.074	830	---	---	835	120	35
1	.064	730	770	920	1220	540	30
2	.069	760	835	1090	1250	450	30
4	.066	800	875	1550	1550	400	32
6	.077	720	---	---	830	175	35
8	.062	690	950	---	950	200	35

## Notes:

1. Curing Agent = dicumyl peroxide
2. Phr = parts per hundred parts of resin

TABLE 6

RELAXATION OF POLYETHYLENE COMPOUNDS AT 250°F<sup>1</sup>

Samples Press-Cured 30 Minutes at 325°F, Oven-Cured 1 Hour at 300°F  
Applied Load-10 Pounds per Square Inch

Curing Agent <sup>2</sup> , Phr	Elongation, %, After					Tension Set, % <sup>3</sup>
	3 Min	5 Min	40 Min	13 Hrs	24 Hrs	
0	Completely Deformed	---	---	---	---	---
1	---	250	Ruptured (@ 300%)	---	---	6
2	---	12	37	Ruptured (@ 87%)	---	18
4	---	12	12	12	25	37
6	---	6	6	6	12	12
8	---	6	6	6	6	6

## Notes:

1. Selected data; complete data are indicated in Figures 4 to 7.
2. Curing Agent = dicumyl peroxide
3. Percent retained of the total elongation, one hour after release of load

TABLE 7

PROPERTIES OF POLYETHYLENE AND POLYETHYLENE-VISTANEX BLENDS

Press-Cured 30 Minutes at 325°F, Oven-Cured 1 Hour at 300°F

Composition	Curing <sup>1</sup> Agent, Phr	Tensile, psi	Elongation, %	Hardness Shore "D"	Elongation %, After <sup>2</sup>		Acid Pen. Hours <sup>3</sup>
					2 Min	24 Hrs.	
100 PE	0	855	120	32	Completely Deformed	--	8
"	4	1400	400	35	---	15	9
"	8	900	200	35	---	4	10
60 PE, 20 Vist	0	865	550	30	Completely Deformed	--	35
"	4	1415	425	29	---	15	68
"	8	1270	400	29	---	12	58
60 PE, 40 Vist	0	630	400	22	Completely Deformed	--	27
"	4	450	280	17	---	20	37
"	8	740	300	17	---	12	41

## Notes:

1. Curing Agent = dicumyl peroxide
2. Suspended at 250°F under applied load of 10 psi for the period indicated.
3. K-Cell penetration, white fuming nitric acid, hours to passage of 2.5 grams of acid per square meter of exposed area.

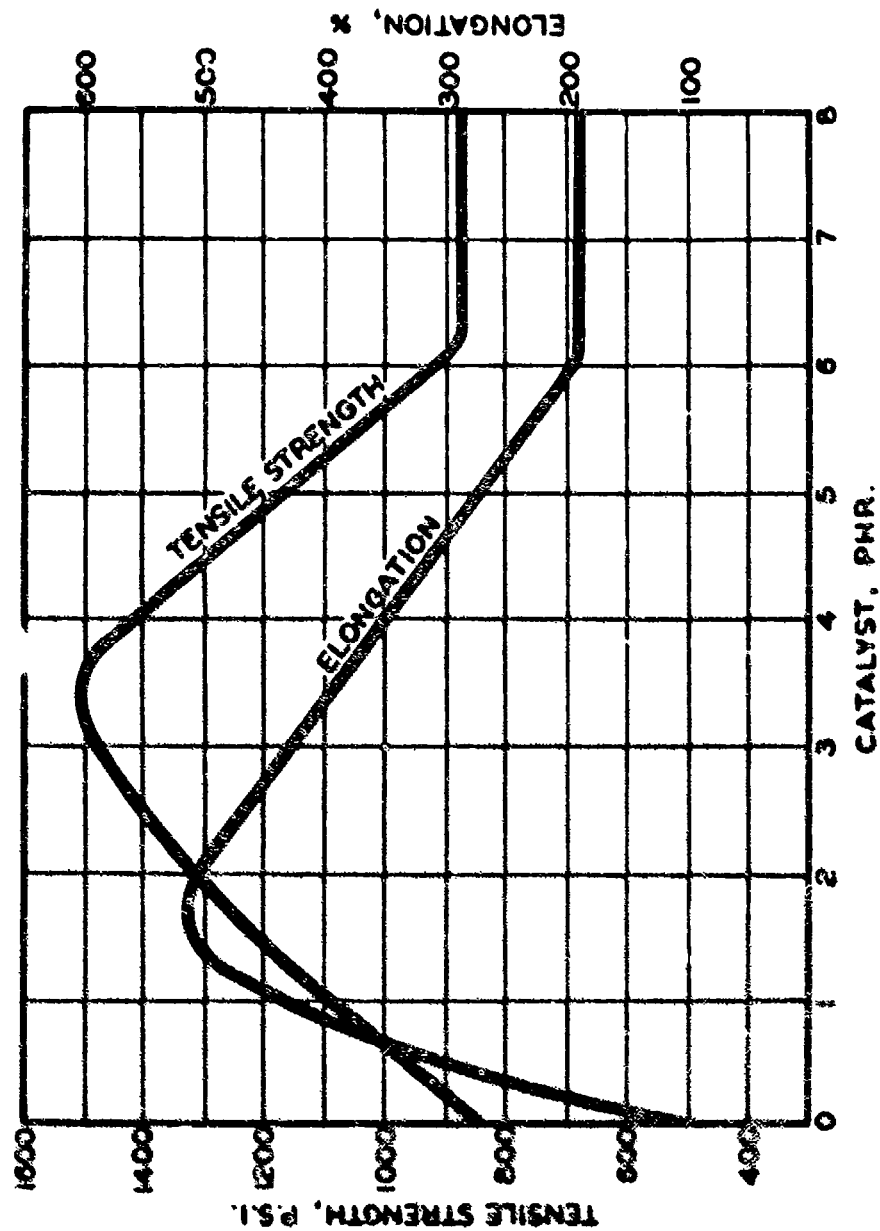


FIG.4 EFFECT OF CATALYST ON TENSILE STRENGTH AND ELONGATION OF POLYETHYLENE

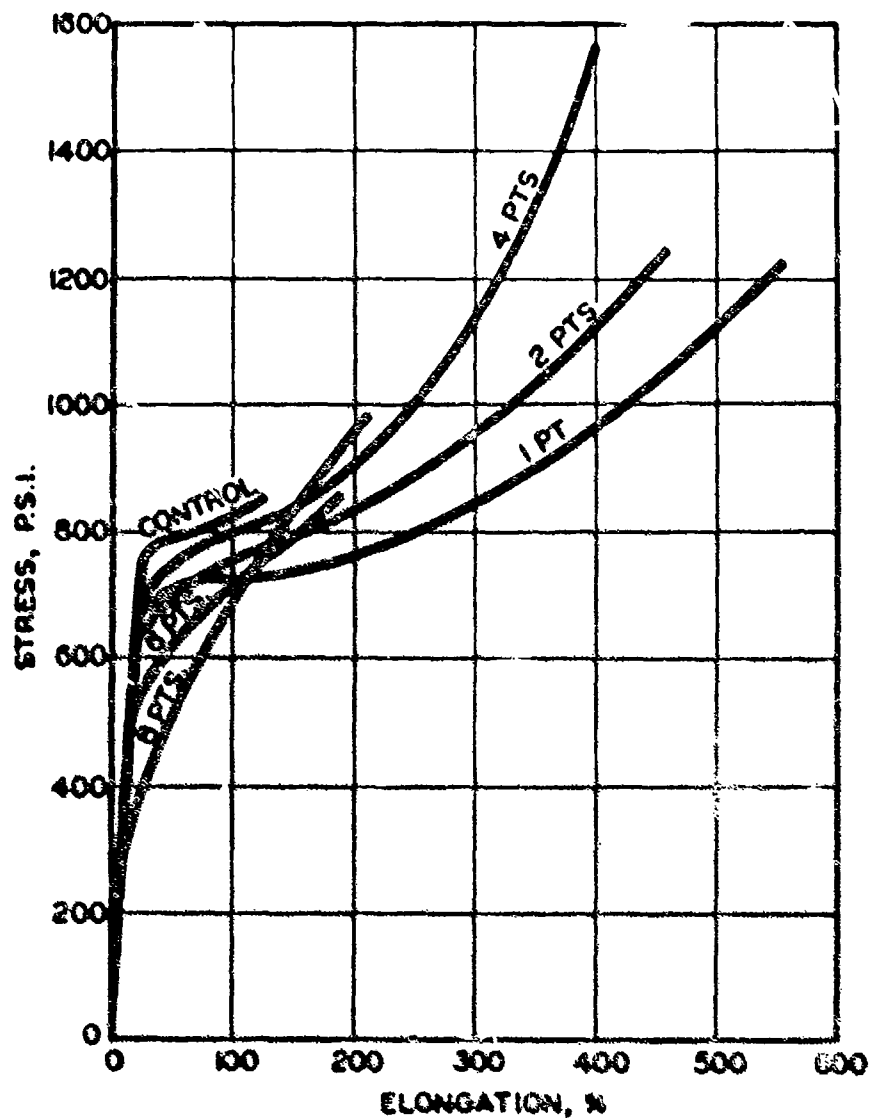


FIG. 5 EFFECT OF CATALYST ON  
STRESS-STRAIN CURVE  
FOR POLYETHYLENE

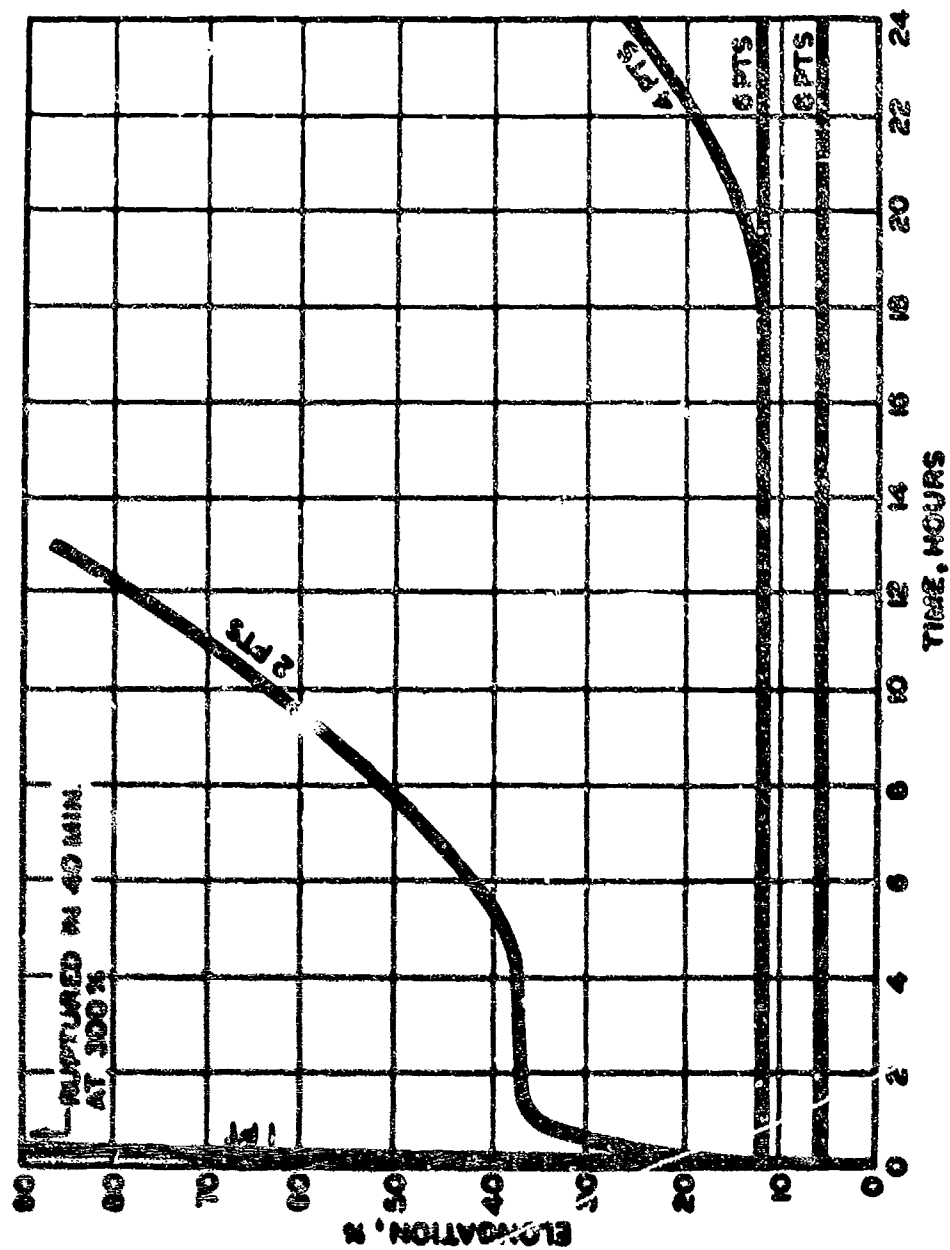


FIG. 6 EFFECT OF CATALYST ON ELEVATED TEMPERATURE RELAXATION OF POLYETHYLENE

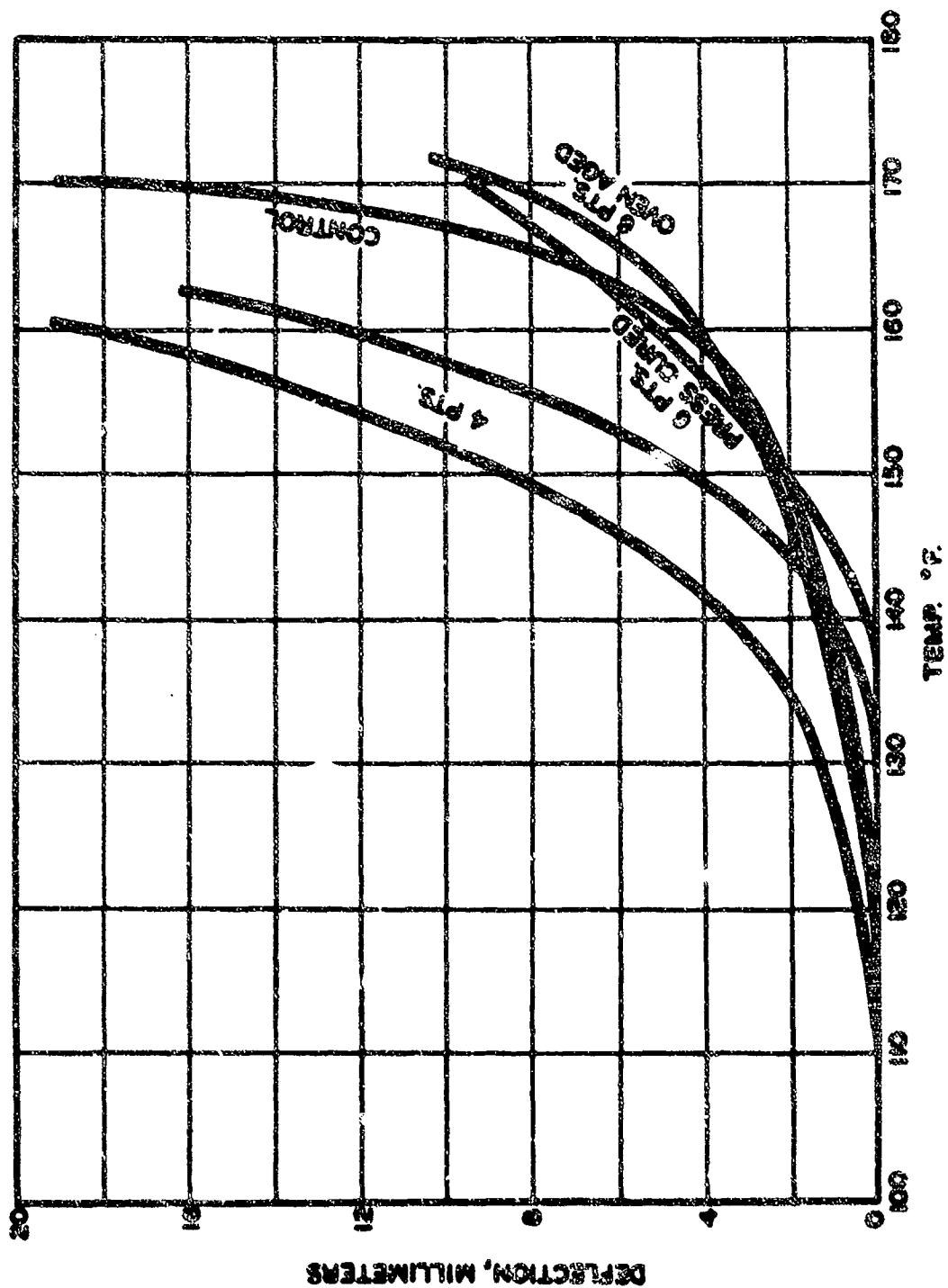


FIG. 7 SOFTENING POINT OF POLYETHYLENE COMPOUNDS

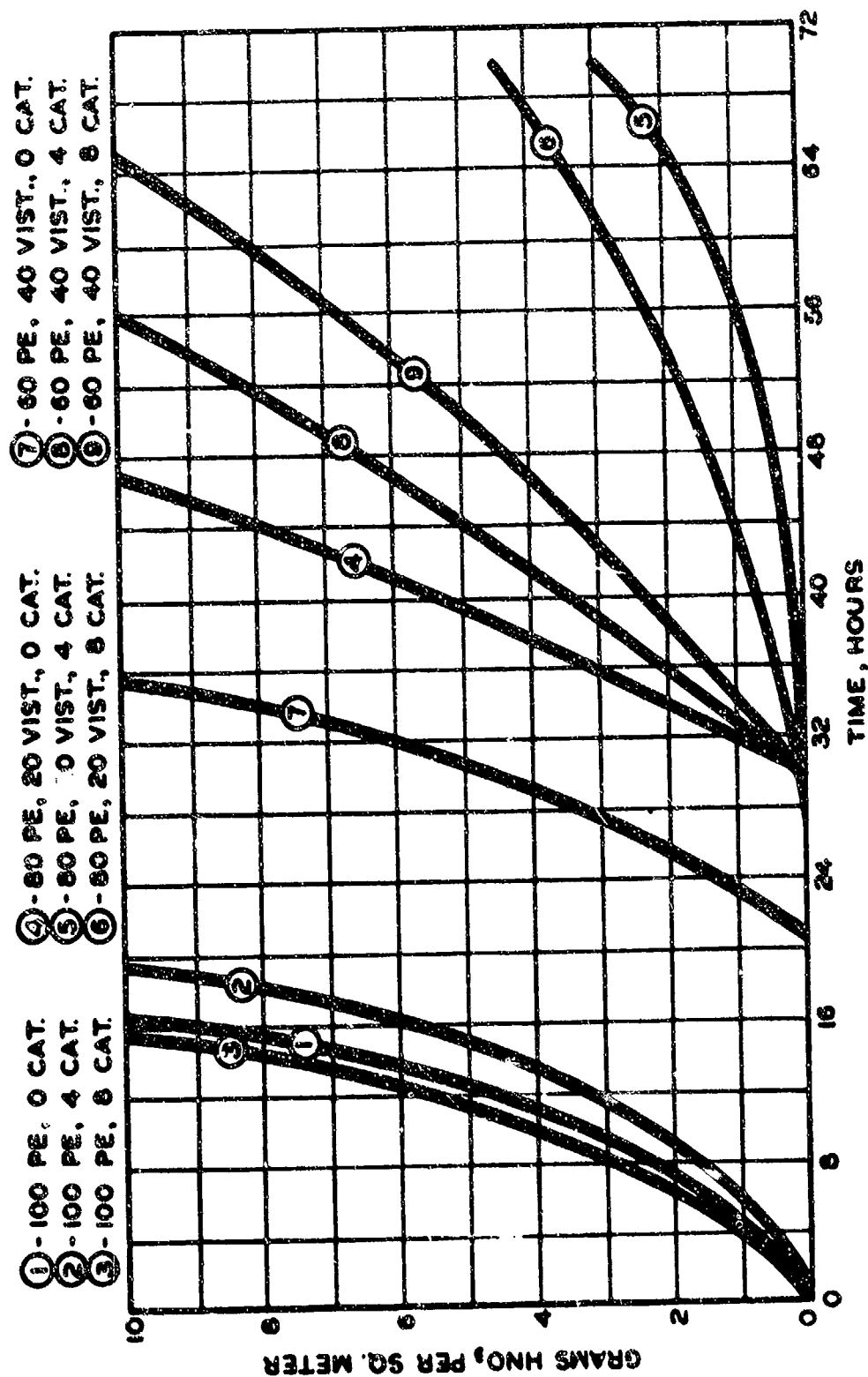


FIG. 8 H-CELL PENETRATION, POLYETHYLENE AND POLYETHYLENE-VISTANEX BLENDS.

## Experiment 8: Global Insulation Tests

**Object:** The purpose of this experiment was (1) to determine the insulation properties of various fabrics when instantaneously exposed to radiant heat at 1000°F, the temperature on the back of the fabric being determined after exposure for 10 seconds, and (2) to determine the maximum temperature reached on the back of the fabric and the time taken to reach this temperature.

**Results:** The presence of a highly reflective aluminum surface was found to be the most important feature for protection against radiant heat (Figure 15). An aluminum foil surface (Rayfoil) was somewhat superior to a vacuum deposited aluminum surface (samples 162-165) which, however, was an excellent heat reflector.

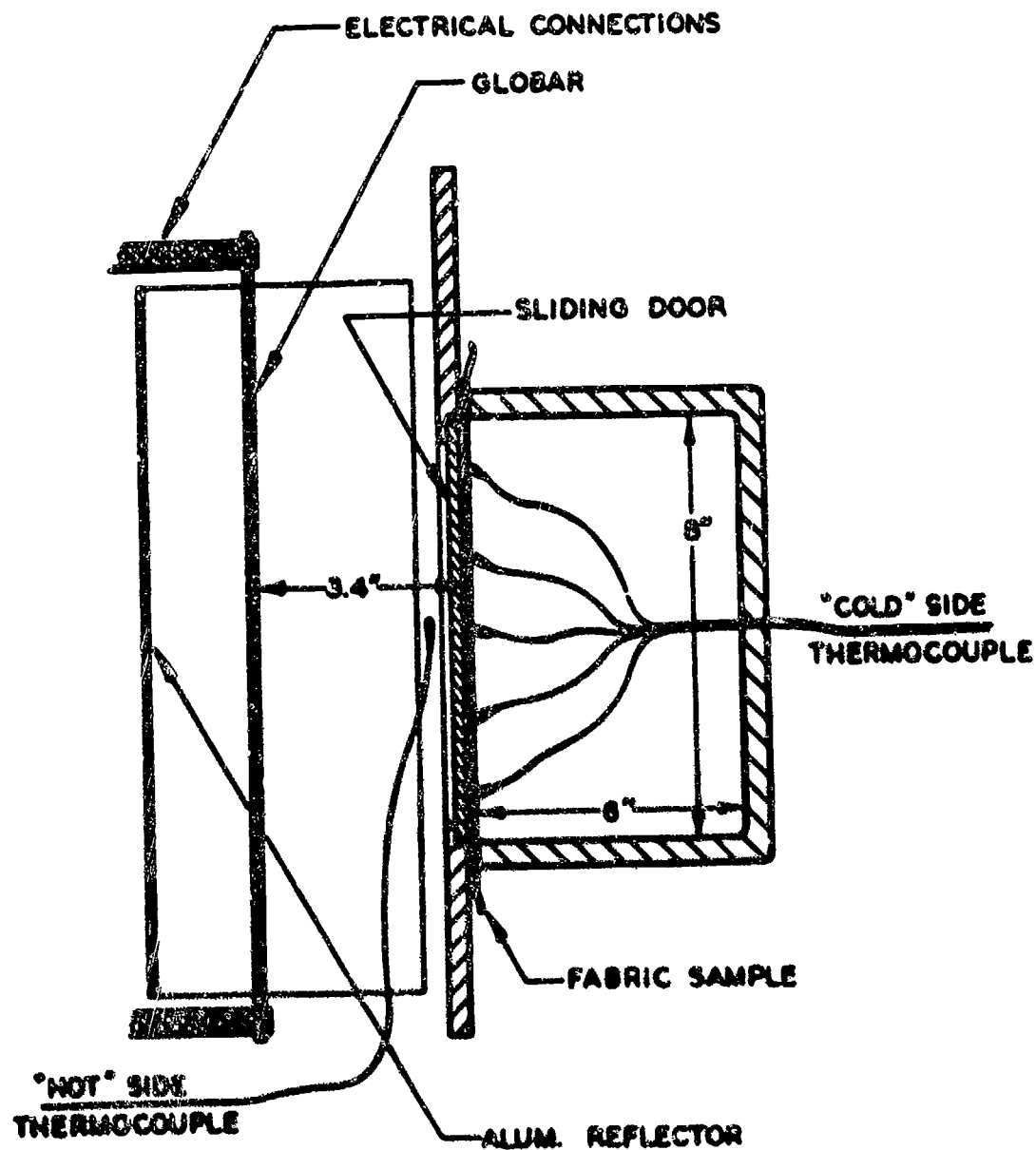
The outstanding samples in the group were those consisting of silicone rubber sponge 0.100 inch or greater in thickness with a vacuum deposited aluminum reflective surface (samples 171, 172, and 173). These showed only a 25°F rise in temperature on the side opposite to that exposed to 1000°F radiant heat for 10 seconds.

The application of a thin (0.002 inch) polymeric coating on the face of the reflective aluminum surface (samples 174, 176, 178 and 179) reduced the reflection of heat considerably. The aluminum-pigmented polymeric coatings (samples 177 and 181) absorbed more heat than the polymer-coated aluminum surfaces, but were still more reflective than uncoated glass fabric surfaces (samples 166 and 167; also compare 180 and 161).

**Materials:** The fabrics used were as follows (thicknesses and weights shown in Table 8). They were prepared as indicated in Experiments 5 and 6:

- 161. Asbestos fabric, Johns-Manville No. WE-5011
- 162. Rayfoil, 0.001 inch aluminum foil adhered to glass fabric.
- 163. Vacuum-deposited aluminum on No. 116 glass fabric (denoted "Vacal" below, and in Table 8).
- 164. Vacuum-deposited aluminum on a lightweight asbestos-glass-cotton fabric, plain weave.
- 165. Vacuum-deposited aluminum on a heavier asbestos fabric, herringbone weave.

166. Glass fabric (No. 116), with a silicone sponge backing (Compound No. 233, Experiment 2), thickness 0.032 inch.
167. Same as #166, except thickness 0.063 inch.
- 168A. Fabric #163 (Vacal) with a silicone sponge backing (compound No. 233, Experiment 2), thickness 0.018 inch.
- 168B. 169A, 169B. Same as #168A, slight differences in thickness and weight (Table 8).
170. Same as #168A, except thickness 0.057 inch.
171. Same as #168A, except thickness 0.099 inch.
172. Same as #168A, except thickness 0.100 inch.
173. Same as #168A, except thickness 0.261 inch.
- 174A. Same as #168A, except a coating of clear Polyfluoron (0.002 inch) on the aluminum face, and overall thickness 0.044 inch.
- 174B. Same as #174A, except overall thickness 0.058 inch.
175. Same as #168A, except a coating of clear Kel-F elastomer gum (0.002 inch) on the aluminum face, and overall thickness 0.045 inch.
176. Same as #168A, except a coating of clear cured polyethylene (0.002 inch) on the aluminum face, and overall thickness 0.052 inch.
177. Same as #166, except a coating of aluminum pigmented Polyfluoron (0.002 inch) on the glass fabric face, and overall thickness 0.040 inch.
181. Same as #166, except a coating of aluminum pigmented cured polyethylene (0.002 inch) on the glass fabric face, and overall thickness 0.040 inch.
180. Same as #181, except a coating of aluminum pigmented Polyfluoron (0.040 inch) on one side.
178. Same as #164, except a coating of clear Polyfluoron (0.002 inch) on the aluminum face.
179. Same as #165, except a coating of clear Polyfluoron (0.002 inch) on the aluminum face.



**FIG.9 GLOBAR RADIANT HEAT EXPOSURE TEST**



FIG. 10 PHOTOGRAPH OF GEARING APPARATUS

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Procedure: A Globar heater (Figure 9 and 10) was prepared, similar to one described in Specification MIL-C-8240 (USAF). The base of the heater was of Transite and Marinite, upon which was mounted a vertical frame of Transite, 14 x 16 inches with a 6 x 8 inch opening in it, and the opening fitted with a sliding gate. At a distance of 3.4 inches from the aperture was mounted a vertical Globar, partially surrounded by an aluminum reflector whose horizontal cross section formed half of an ellipse of formula  $(3x)^2 + (4.5y)^2$ . The upper part of the heater was covered by a hood made of thin aluminum, in order to minimize chimney effects. The fabric sample was attached across the 6 x 8 inch opening of a box of inside dimensions 6 x 8 x 6 inches. Inside the box, and touching the back (non-reflective side) of the fabric were five fine-wire (No. 30 iron-constantan) thermocouples connected in parallel and to a pyrometer. On the Globar side of the gate in the vertical Transite frame, a heavier thermocouple (No. 24 iron-constantan) was mounted one-quarter inch in front of the gate.

In operation, the fabric sample was attached across the opening of the box and the box and sample held apart from the Transite frame and Globar. The Globar was heated (about 80 volts and 20-23 amperes, yielding approximately 2600°F at the Globar surface) and the voltage adjusted to show 1000°F on the thermocouple mounted in front of the gate. The sample (attached to the box) was then pressed manually against the opening in the Transite frame, and the gate opened. The temperature on the cold side was noted after 10 seconds, at which time the box and sample were removed from the frame, and the gate closed. The maximum temperature reached on the back of the sample was recorded and the total time required to reach that temperature was noted.

Data: The data for the various fabrics in this test are presented with the 1000°F steam test data in Table 8. The Globar data are shown graphically in Figures 11 to 15.

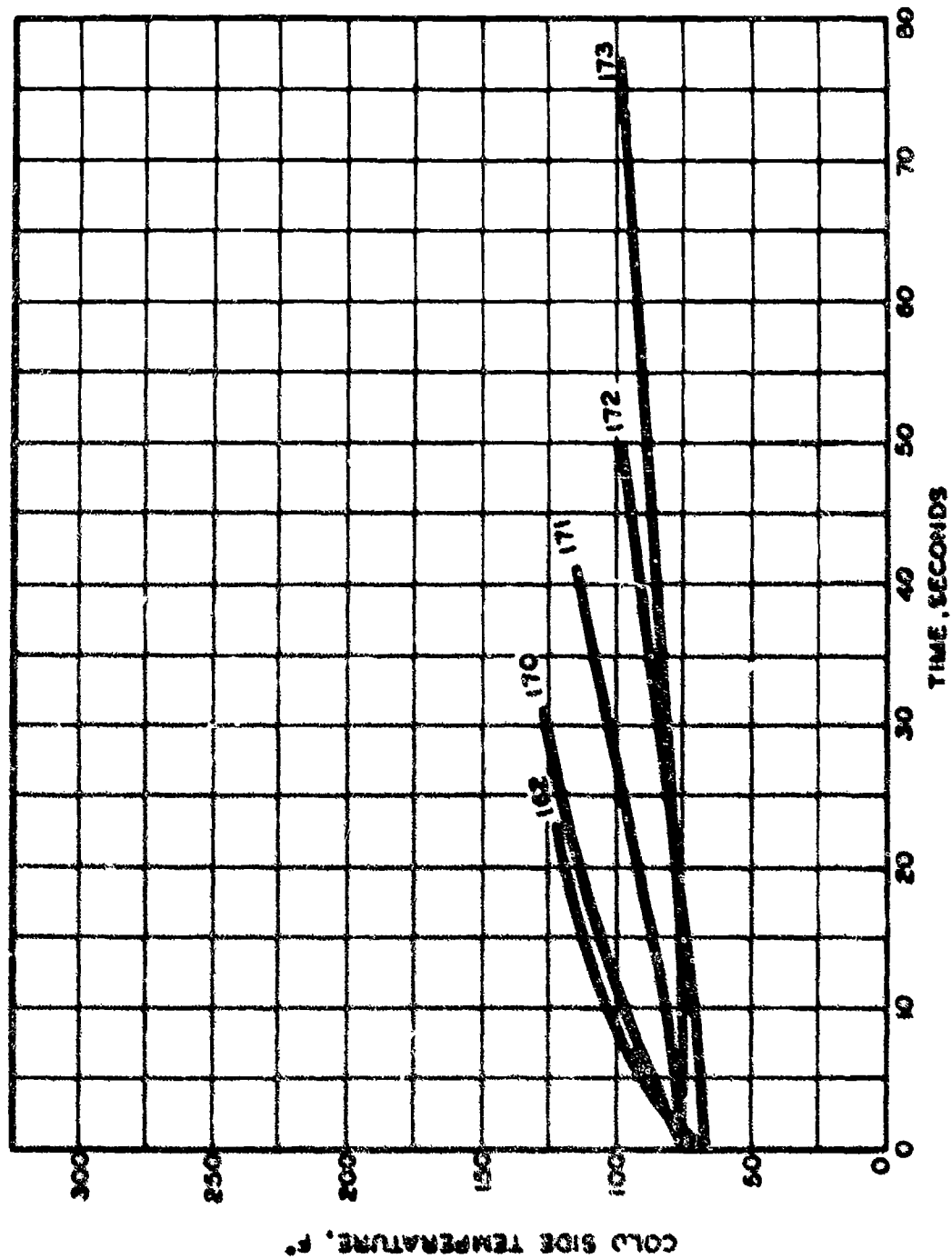
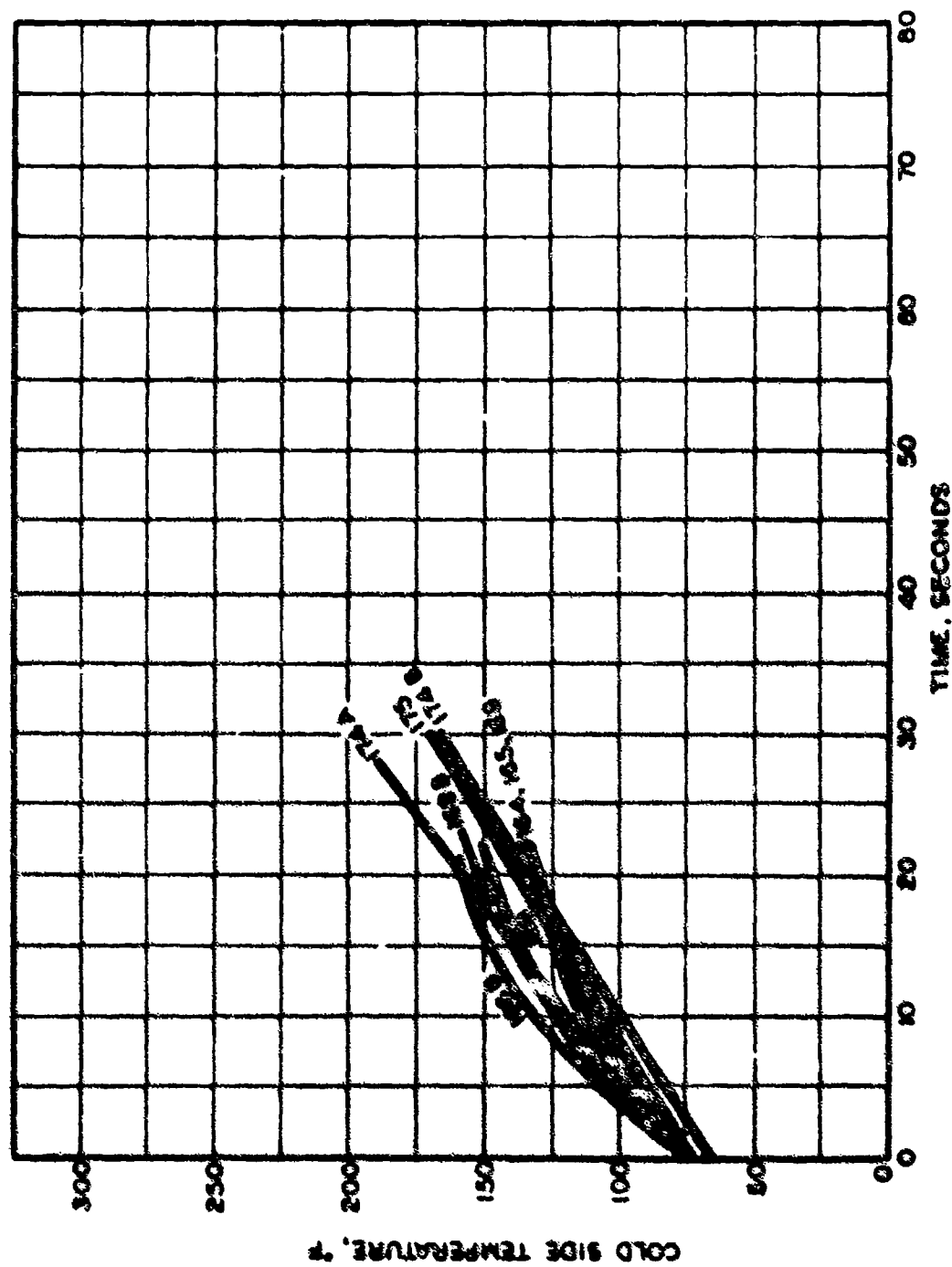


FIG. II GLOBAR TESTS, GROUP I.



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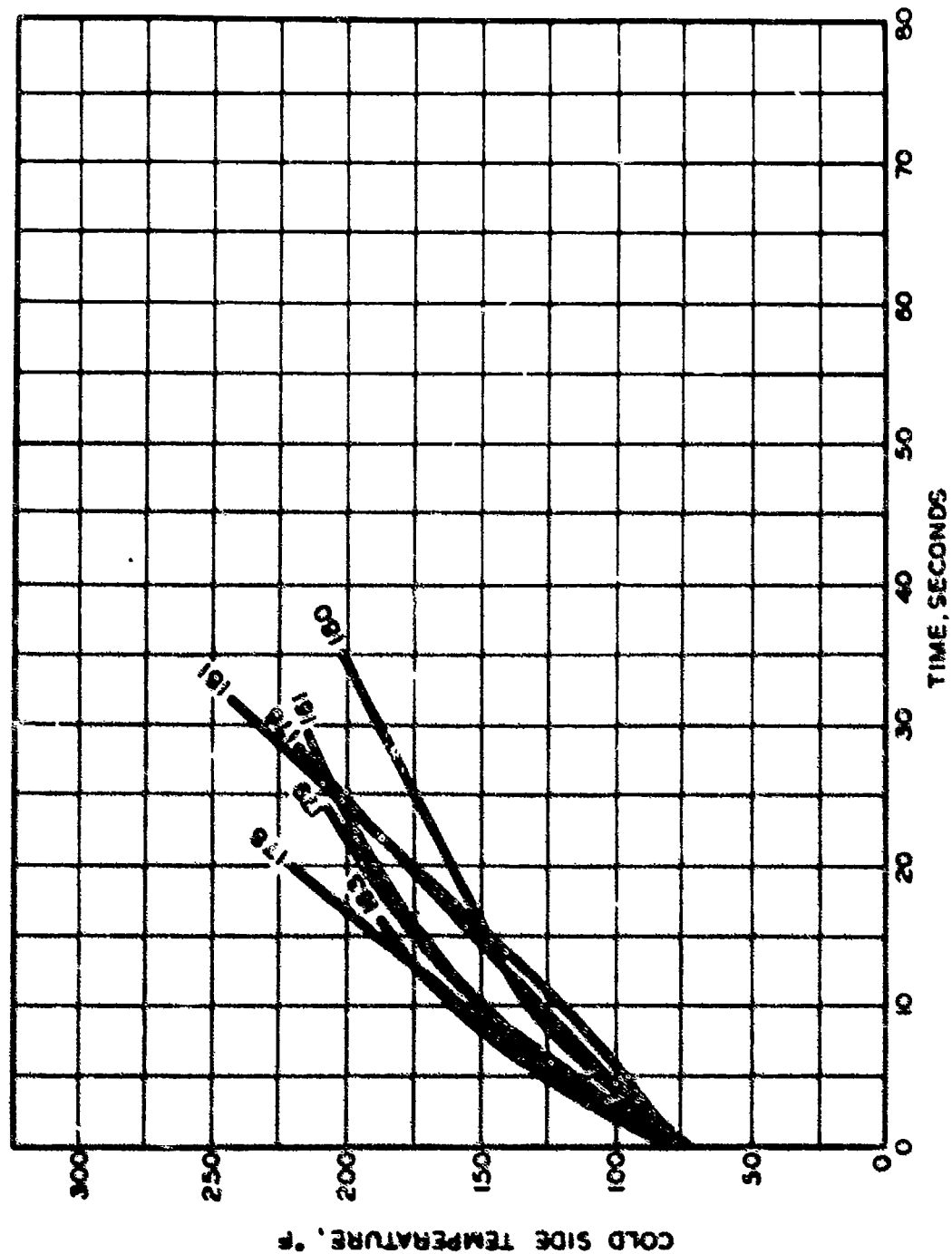


FIG. 13 GLOBAR TESTS, GROUP 3.

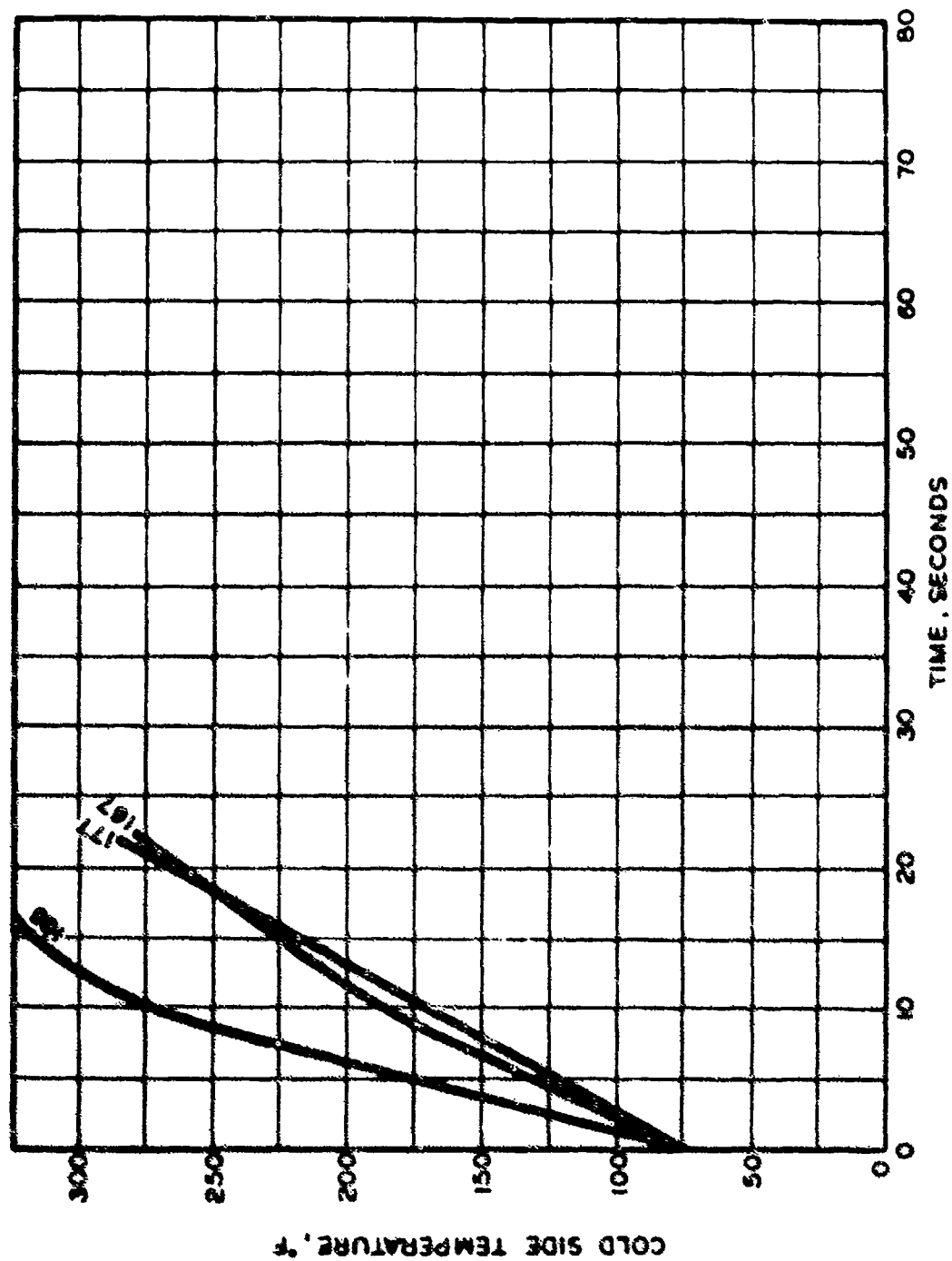


FIG. 14 GLOBAR TESTS, GROUP 4.

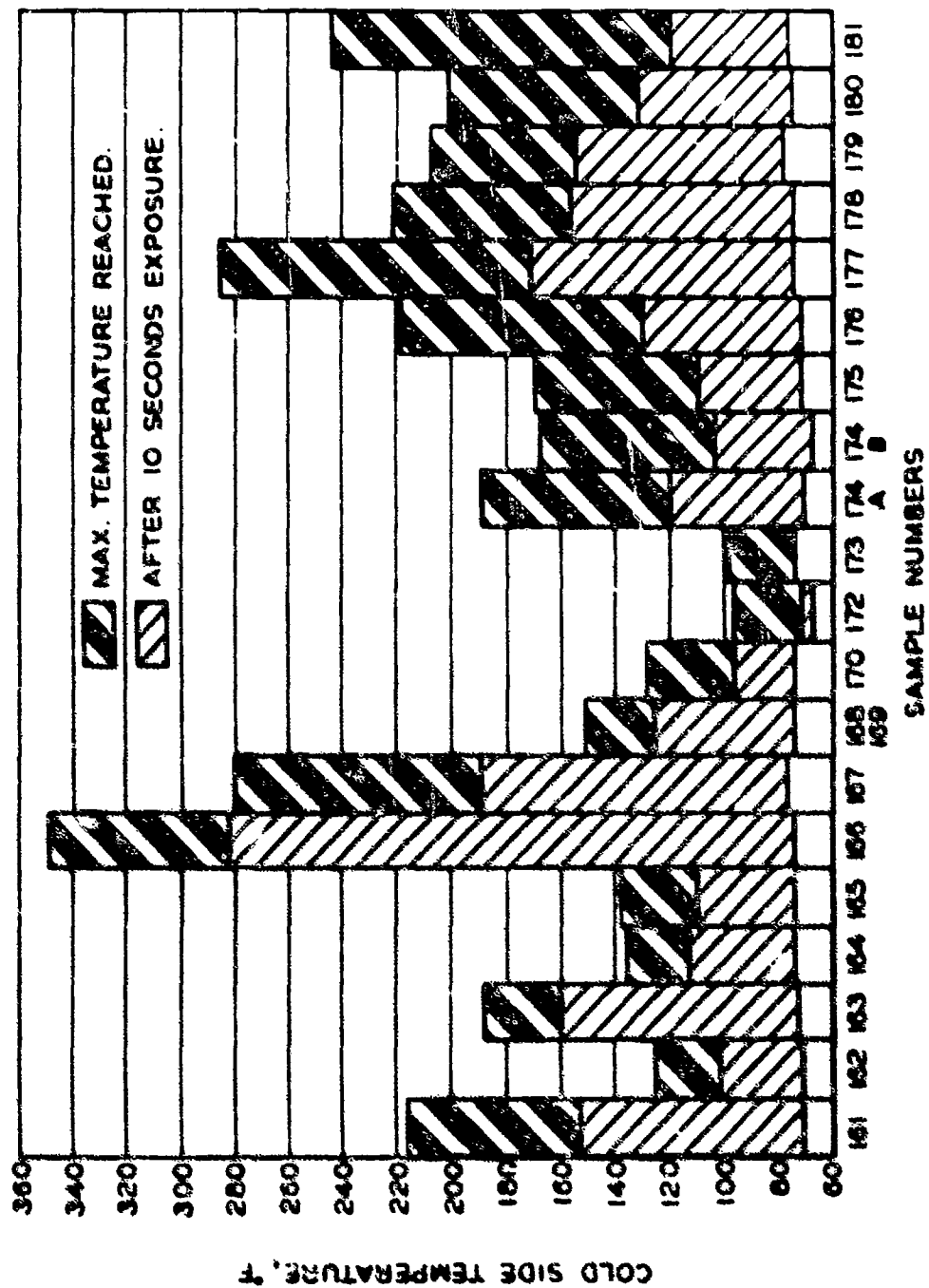


FIG. 15 GLOBAR TESTS, COMPOSITE

#### Experiment 9: 1000°F Steam Insulation Tests

**Object:** The purpose of this experiment was (1) to determine the insulation properties of various fabrics when instantaneously exposed to superheated steam at 1000°F, the temperature on the back of the fabric being determined after exposure for 10 seconds; (2) to determine the maximum temperature reached on the back of the fabric and the time taken to reach this temperature; and (3) to determine the amount of superheated steam which passed through the fabric, recorded as grams of water per square meter of fabric.

**Results:** The data indicate that the best insulating material against contact with 1000°F steam was a thick non-porous material having low heat conductivity. The presence of a highly reflective surface was of less importance than the thickness, but the effect of the reflective surface was quite noticeable (Figure 22).

All of the ordinary fabric samples without a silicone rubber sponge backing, except "Rayfoil" (0.001 inch aluminum foil on glass fabric), allowed passage of a significant amount of water vapor. Only the thinnest sponge-fabric samples (0.020 inch) allowed passage of a measurable amount of water vapor, and these allowed only 2.0 grams per square meter of exposed area. The water vapor transmission of the "Vacal" (vacuum-deposited aluminum on No. 116 glass fabric) was also low.

The outstanding samples of the group were the thick sponge-fabrics (0.10 and 0.26 inch, weighing only 1.5 and 3.1 pounds per square yard, respectively) which showed maximum temperature rises on the back side of only 55° and 50° after ten seconds' exposure to 1000°F steam.

**Materials:** See the list of fabrics described under Experiment 8. The same fabrics were tested in this experiment (Table 8).

**Procedure:** Figure 16 is a detailed drawing of the equipment used in this experiment. Basically, the equipment is best described as having two major components. The first consisted of a low-pressure steam generator, a heat exchanger and a flanged bell. A gate immediately in the rear of the flange allowed the entire bell chamber to be preheated to 1000°F by superheated steam. A wire-screen diffuser was introduced in the path of the steam at the entrance to the bell to prevent a jet effect. The second component consisted of a drying train for the air-intake and an absorption train for the moisture determination, both connected to a second flanged bell. The oven-dried sample was held tightly against

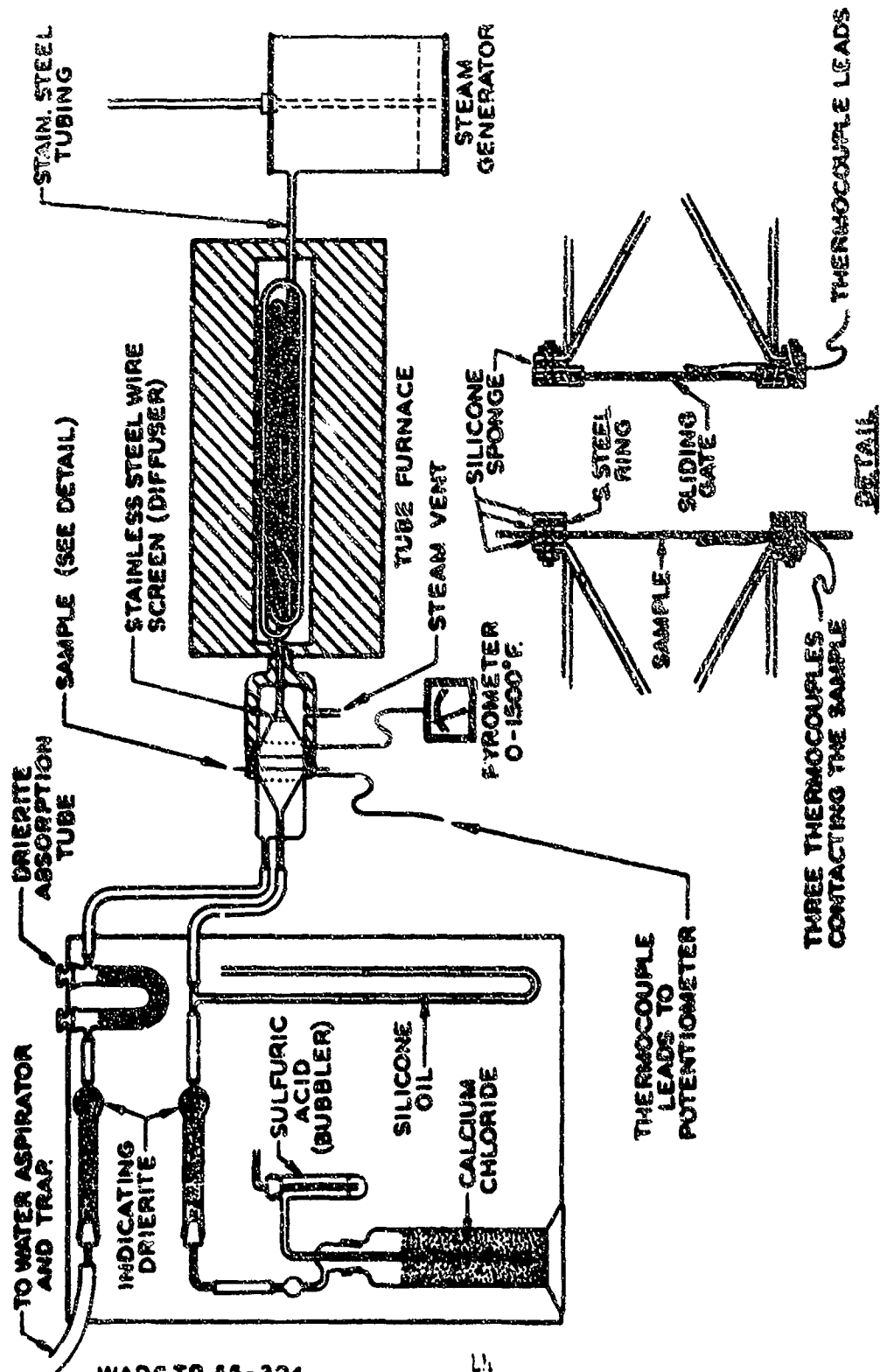
this flange by means of a flat steel ring with four lug bolts. Securely cemented to both sides of this ring and also to the face side of the bell flange were silicone sponge rubber gaskets to insure an air-tight seal. The diameter of the exposed sample was 2 5/8 inches.

In operation the aspirator was turned on, and two blank determinations were run on the sample to insure against any moisture which might have entered the bell while the sample was being installed. It should be noted here that the bell and sample were not in contact with the other bell during the blank determinations, but were hanging downward and resting on a perforated support. Meanwhile, the steam temperature was raised to 1000°F, and the steam bell chamber was allowed to come to equilibrium.

The sample (mounted in its bell) was then pressed manually against the other bell and the gate was opened. The temperature on the cold side was noted after 10 seconds, at which time the bell was removed from the steam source. The maximum temperature obtained on the back of the sample was recorded and the total time required to reach this temperature was noted. A single No. 24 iron-constantan thermocouple connected to a pyrometer was used to indicate the temperature in the steam bell chamber; and three No. 30 iron-constantan thermocouples connected in parallel and to a potentiometer were used to indicate the average temperature on the cold side of the fabric. Figure 17 shows photographs of the apparatus. The aspirator was run for a total of 20 minutes to insure the absorption of all moisture which might have penetrated the fabric. A value of 2.5 grams per square meter of fabric was selected as being the maximum allowable penetration of super-heated vapor (see Discussion Section).

Data: See Table 8 and Figures 18 to 22.

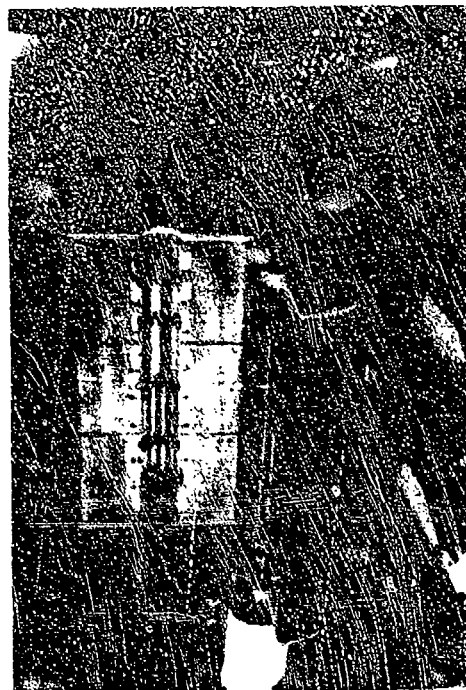
Discussion: For protective clothing use, a value of 2.5 grams of fuming nitric acid per square meter of fabric was selected in an earlier investigation (1) by this company as being the maximum allowable penetration. In the present project, it was assumed that should ignition take place the superheated vapors could contain an appreciable amount of this acid. Consequently, the steam tests were performed with the assumption that all of the vapor could be fuming nitric acid, and on this basis the above figure was selected as the maximum allowable penetration of steam.



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FIG. 16 1000°F STEAM EXPOSURE TEST



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FIG. 17 PHOTOGRAPH OF STEAM APPARATUS

TABLE 8

HEAT- AND ACID-RESISTANT FABRIC EVALUATION

Sample No.	Description	Thick- ness, Inch.	Weight, lb./yd. <sup>2</sup>	Globar (1000° F.)					Steam (1000° F.)					Vapor Trans. G./m. <sup>2</sup>	Insul. Rating <sup>2</sup> Globar Ste.
				Temp. °F.		Time to			Temp. °F.		Time to				
				Init.	Sec.	Max.	Max., Sec.	Init.	Sec.	Max.	Max., Sec.				
161	Asbestos Fabric	.090	2.94	72	154	216	29	23	76	180	208	23	81	3	2
162	Rayfill	.008	0.52	72	107	124	23	13	72	200	258	13	0.5	1	3
163	Vacal (Vac.AL. on Glass)	.004	0.23	74	160	187	17	13	78	380	410	13	4.5	3	4
164	Vac.AL.-Asbestos, plain	.026	0.72	75	114	136	22	14	80	285	364	14	46	2	4
165	Vac.AL.-Asbestos, harr.	.040	1.13	75	111	137	24	16	89	227	288	16	62	2	3
166	Glass - Sponge	.032	0.78	75	282	351	16	14	78	285	358	14	--	4	4
167	Glass - Sponge	.063	1.14	77	190	281	22	17	83	190	257	17	0.5	4	3
168A	Vacal - Sponge	.018	0.64	75	125	152	22	15	81	230	280	15	2.0	2	3
168B	" "	.019	0.63	75	135	160	21	15	87	280	335	15	--	2	4
169A	" "	.018	0.63	75	135	137	20	16	90	230	283	16	--	2	3
169B	" "	.021	0.66	75	126	158	23	17	93	207	263	17	2.0	2	3
170	" "	.057	1.08	75	97	128	31	22	92	158	227	22	0.5	1	2
171	" "	.099	1.52	76	83	114	41	30	90	115	165	30	0.5	1	1
172	" "	.100	1.53	68	72	97	50	38	95	105	160	38	0.5	1	1
173	" "	.261	3.10	75	75	99	77	75	95	95	145	75	0.5	1	1
174A	P.P.-Vacal-Sponge	.044	1.02	71	120	189	28	20	78	168	278	20	0.5	2	3
174B	P.P.-Vacal-Sponge	.058	1.18	66	103	168	30	23	93	197	288	23	"	2	3
175	KFB-Vacal-Sponge	.045	1.07	72	110	170	30	22	78	170	267	22	"	2	3
176	C.P.L.-Vacal-Sponge	.032	1.06	72	130	219	28	18	88	178	288	18	"	3	3
177	Al.pig.P.C.F.-Glass- Sponge	.040	0.95	75	172	285	22	18	88	200	312	18	"	4	3

TABLE 8 (con't)

## HEAT- AND ACID-RESISTANT FABRIC EVALUATION

Sample No.	Description	Thick- ness, Inch	Weight <sup>1</sup> lb/yd <sup>2</sup>	Glebar (1000° F)			Steam (1000° F)			Vapor Trans. g./m. Globar Steam	Insul. Rating <sup>2</sup>			
				Temp. ° F.		Time to Max. Sec.	Temp. ° F.		Time to Max. Sec.					
				Init.	Sec.		Init.	Sec.						
181	Al. pig. C. P. R.- Glass-Sponge	.070	1.40	77	120	243	32	85	132	240	25	0.5	3	2
180	Al. pig. P. P.-Asbec- tes (161)	.096	3.24	76	132	201	35	92	178	212	22	91	2-3	2
178	P. P.-Vac. Al.-Asbec- tes (164)	.028	0.76	75	157	221	20	92	320	386	13	45	3	4
179	P. P.-Vac. Al.-Asbec- tes (165)	.044	1.24	78	155	209	24	93	190	270	20	30	3	3

1. Overall thickness and weight of the fabric product.

2. Ratings: 1 = Excellent, 2 = Good, 3 = Fair, 4 = Poor.

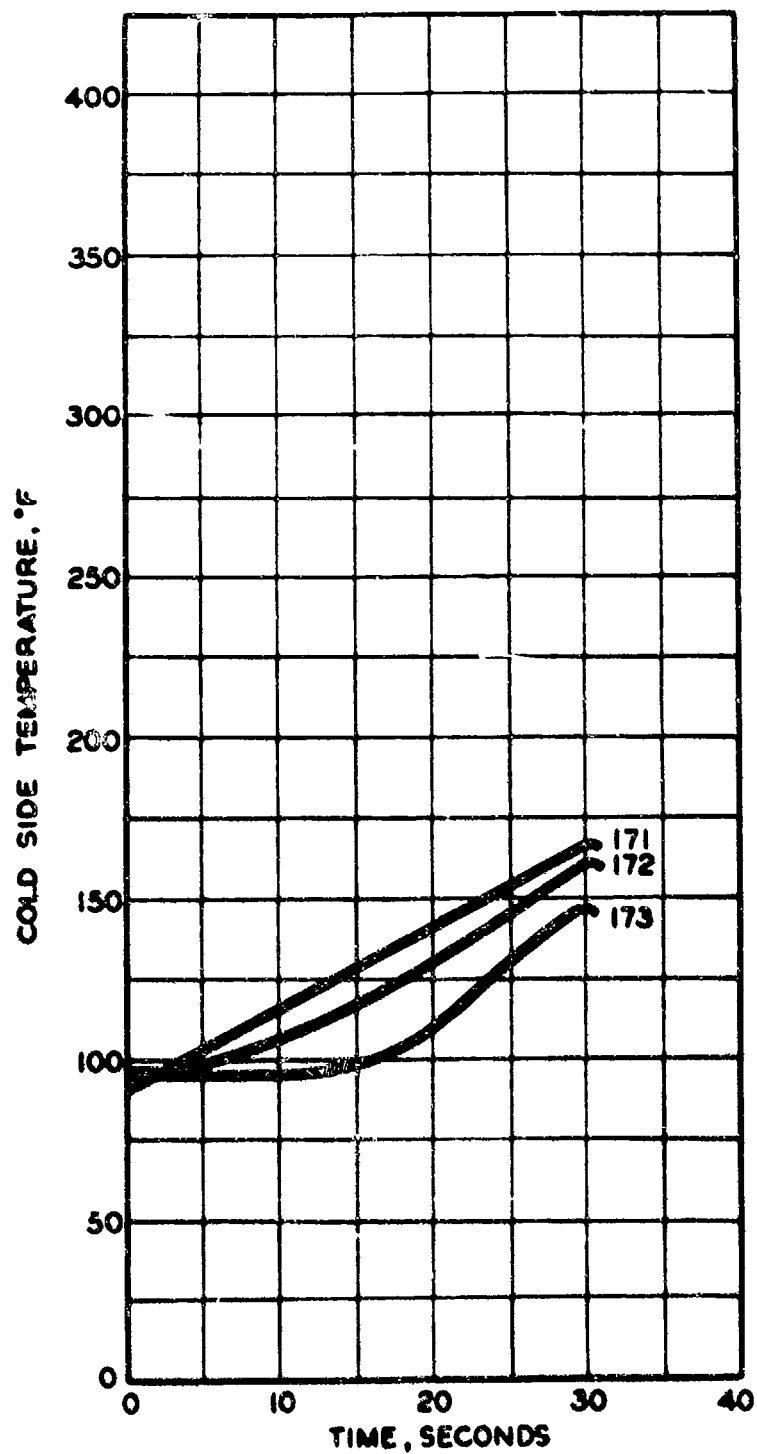


FIG. 18 STEAM TESTS, GROUP I.

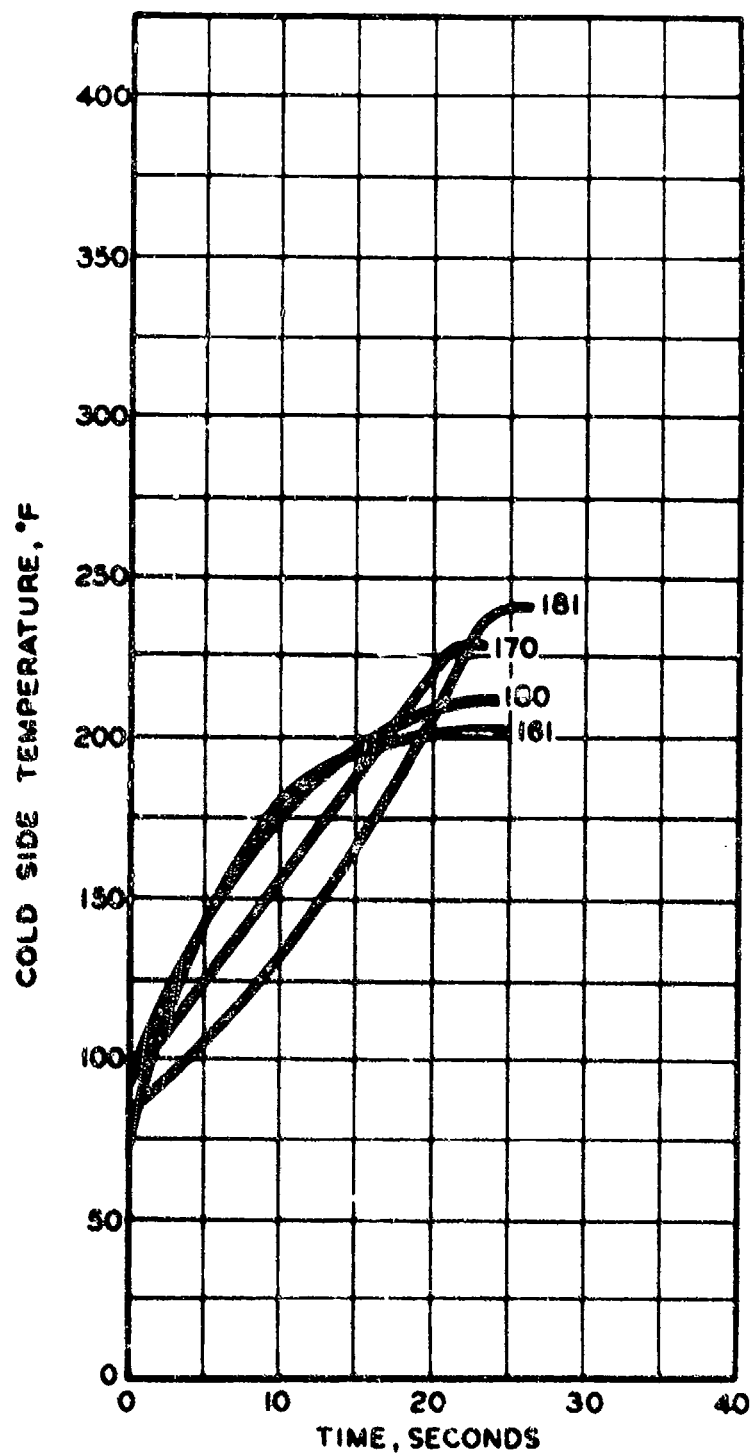


FIG.19 STEAM TESTS, GROUP 2.

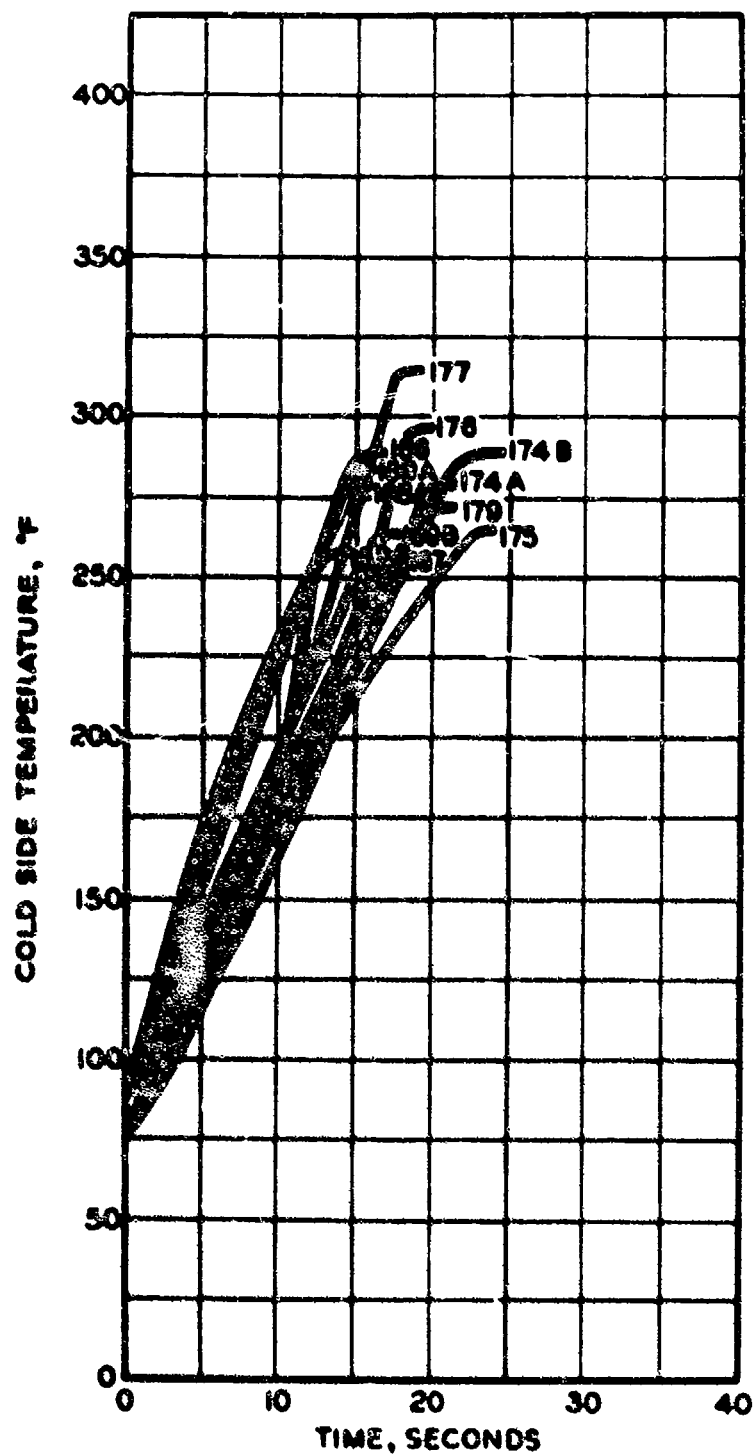


FIG. 20 STEAM TESTS, GROUP 3.

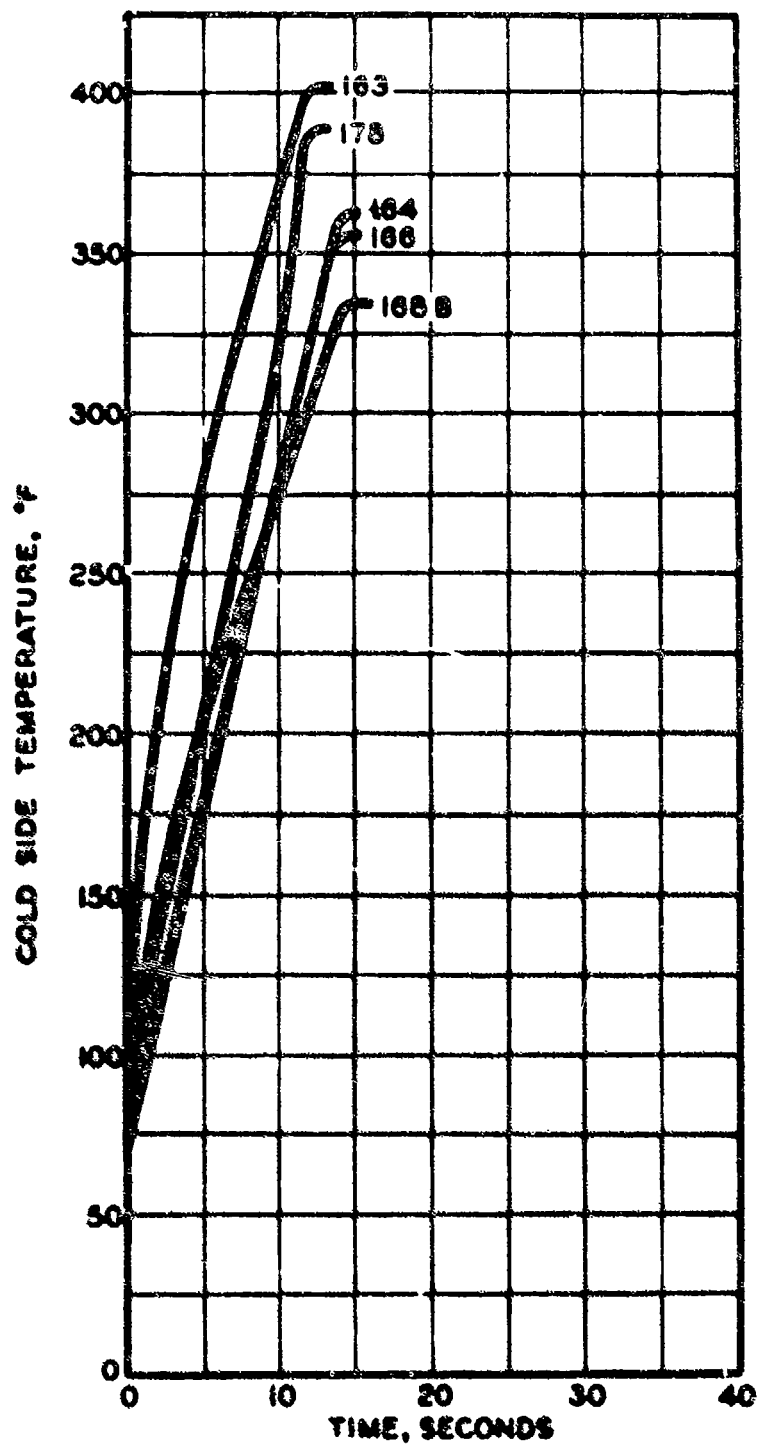


FIG 21 STEAM TESTS, GROUP 4.

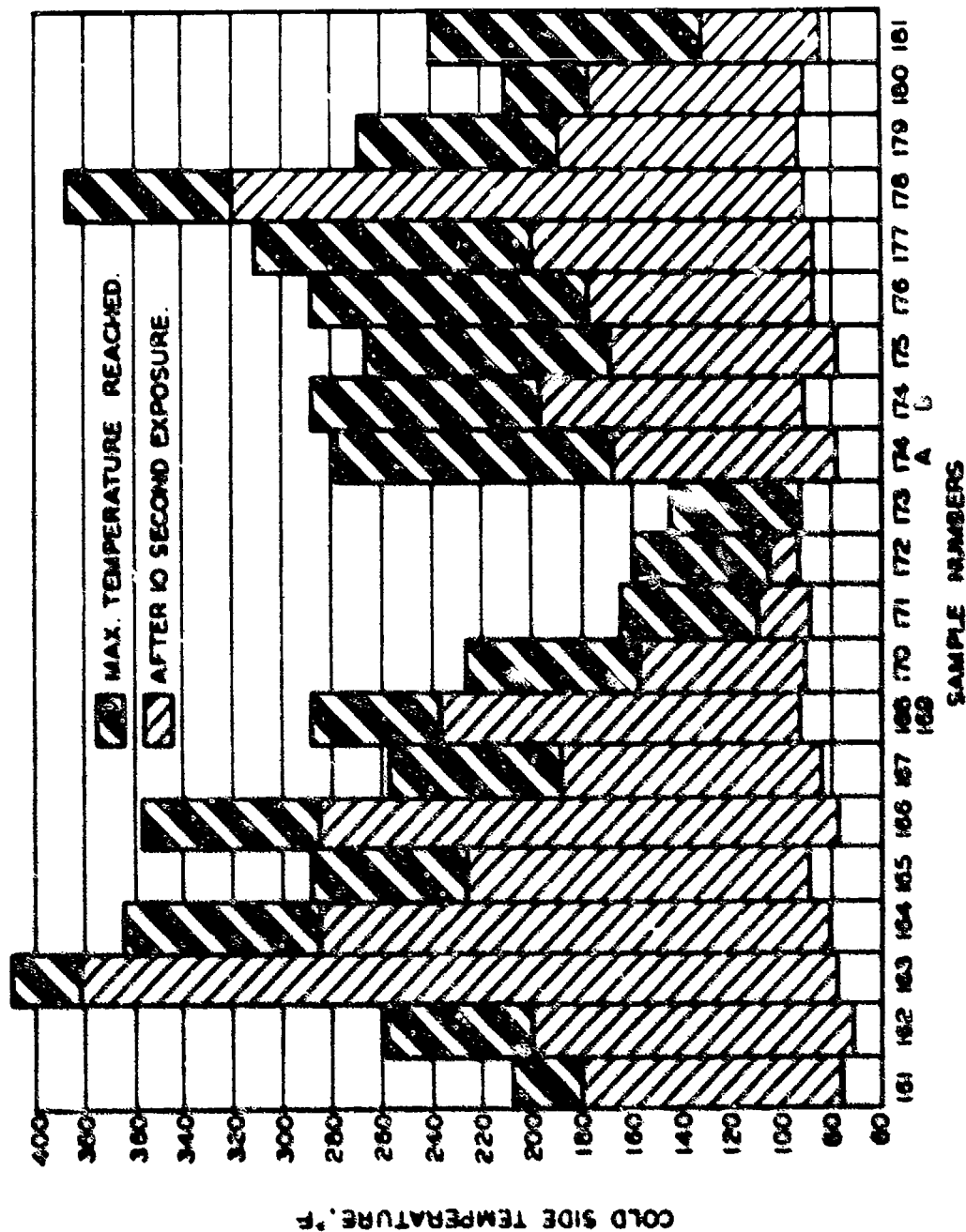


FIG.22 STEAM TESTS, COMPOSITE.

#### Experiment 10: H-Cell Acid-Penetration Tests

**Object:** To compare the acid-resistance of various types of polymer coatings applied on glass fabric (see Experiment 5). Three acid-resistant coating materials, Polyfluoron (polychlorotrifluoroethylene), polyethylene-Vistanex, and Kel-F Elastomer, and two general coating methods (knife and spray) were compared by means of H-Cell acid-penetration tests.

**Results:** Of the three materials tested, Polyfluoron showed considerably better resistance to penetration by white fuming nitric acid than the others. A thin knife-coating (0.0015 inch) on aluminized glass fabric allowed passage of 2.5 grams of nitric acid per square meter of exposed area after 27 hours of exposure (Figure 25). After this length of time, the thin vacuum-deposited aluminum coating was destroyed only in very small spots where apparently a few pinholes were present in the thin, transparent, acid-resistant coating. About 95 percent of the aluminum coating was unharmed.

The thin polyethylene-Vistanex knife-coating (0.002 inch) on aluminized glass fabric showed good resistance to penetration, about 12 hours being required for the passage of 2.5 grams of nitric acid per square meter. The thin Kel-F Elastomer knife-coating (0.0013), also on aluminized glass fabric, showed the least resistance to penetration. Also, in the case of both the polyethylene-Vistanex and the Kel-F Elastomer coatings, there apparently was little adhesion of the polymer coating to the thin aluminum layer, and in samples of each the polymer coating separated out from the fabric in a large blister, resulting in complete destruction of the aluminum reflective layer.

Results obtained with spray-coated Polyfluoron and Kel-F Elastomer on aluminized glass fabric were almost identical with those shown in Figure 25 (average 33 hours for Polyfluoron, 2 hours or less for Kel-F Elastomer). It was not practical to apply the polyethylene-Vistanex blend by solution spraying (Experiment 5).

A second series of samples was prepared by applying aluminum-pigmented polymer coatings on plain glass fabric. Initial coating of pigmented Polyfluoron applied by spraying on the plain glass showed the presence of pinholes. It was found, however, that a thin spray coating (see Experiment 6) followed by two knife-coatings (final coating thickness 0.002 inch) withstood 165 to 200 hours' exposure in the H-Cell before passage of 2.5 grams of nitric acid per square meter of exposed area (Figure 26).

Samples prepared by knife-coating polyethylene-Vistanex and Kel-F Elastomer, (0.002 inch in thickness) pigmented and unpigmented, on plain glass showed the presence of pinholes in H-Cell tests, failing in all cases in two hours or less.

**Materials:** (See Experiment 5 for compounding and application details on the polymer coatings.) Figure 25: Polymer coatings (0.0015-0.002 inch in thickness) knife-coated over vacuum-deposited aluminum on No. 116 glass fabric;

Polyfluoron

Polyethylene-Vistanex (40:60 blend)

Kel-F Elastomer (clear, uncompounded gum)

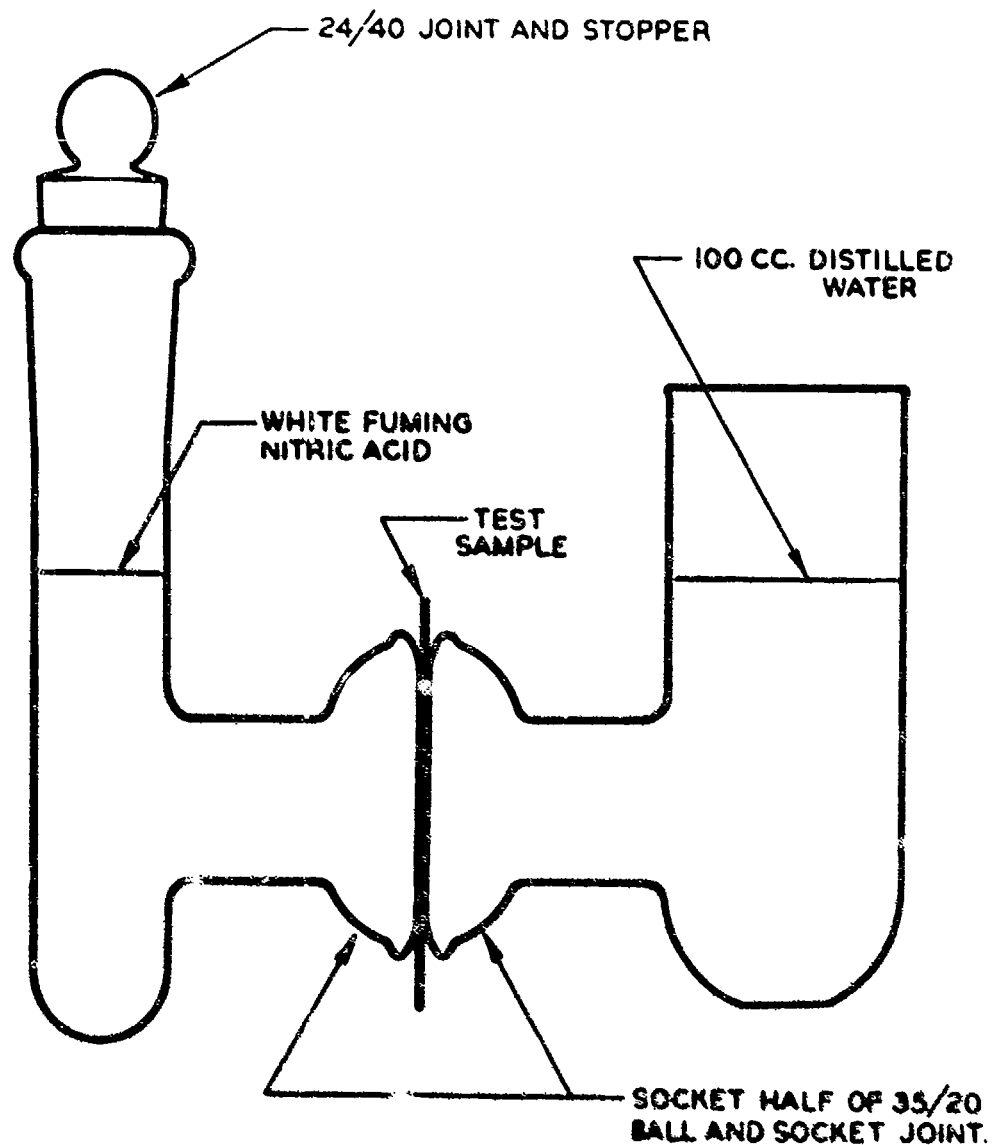
**Figure 26:** Aluminum-pigmented Polyfluoron coating (0.002 inch in thickness) knife-coated on No. 116 glass fabric.

**Procedure:** Duplicate portions of the coated fabric samples described above were mounted as diaphragms in H-shaped cells, which are divided into two sections at the center of the H (see Figure 23). Distilled water was placed in one side of the cell, and white fuming nitric acid in the other. The pH of the water was measured at intervals, and the permeability was calculated from the dimensions of the cell. Figure 24 is a calibration curve relating the measured pH to the permeability in grams per square meter for white fuming nitric acid through a test membrane.

In operation, the sample was clamped between the two sections of the cell with a ball and socket clamp, a butyl rubber gasket being used on the water side. One hundred milliliters of distilled water were pipetted into the distilled water cup, and an initial pH reading was taken by means of a Beckman pH meter. Fuming nitric acid was then poured into the ground-glass stoppered tube, and the pH of the water was measured periodically until the pH fell below 3.7, which is equivalent to a penetration of 2.5 grams of nitric acid per square meter of exposed area. Penetration versus time was plotted to indicate the rate and the time of failure.

**Data:** See Figures 25 and 26.

**Discussion:** The test described above for determining the permeability of various materials to white fuming nitric acid was developed by the Naval Air Rocket Test Station. The method has been described as the H-Cell Test in reports covering previous contract work in this laboratory.



**FIG. 23 H-CELL FOR ACID PENETRATION TEST**

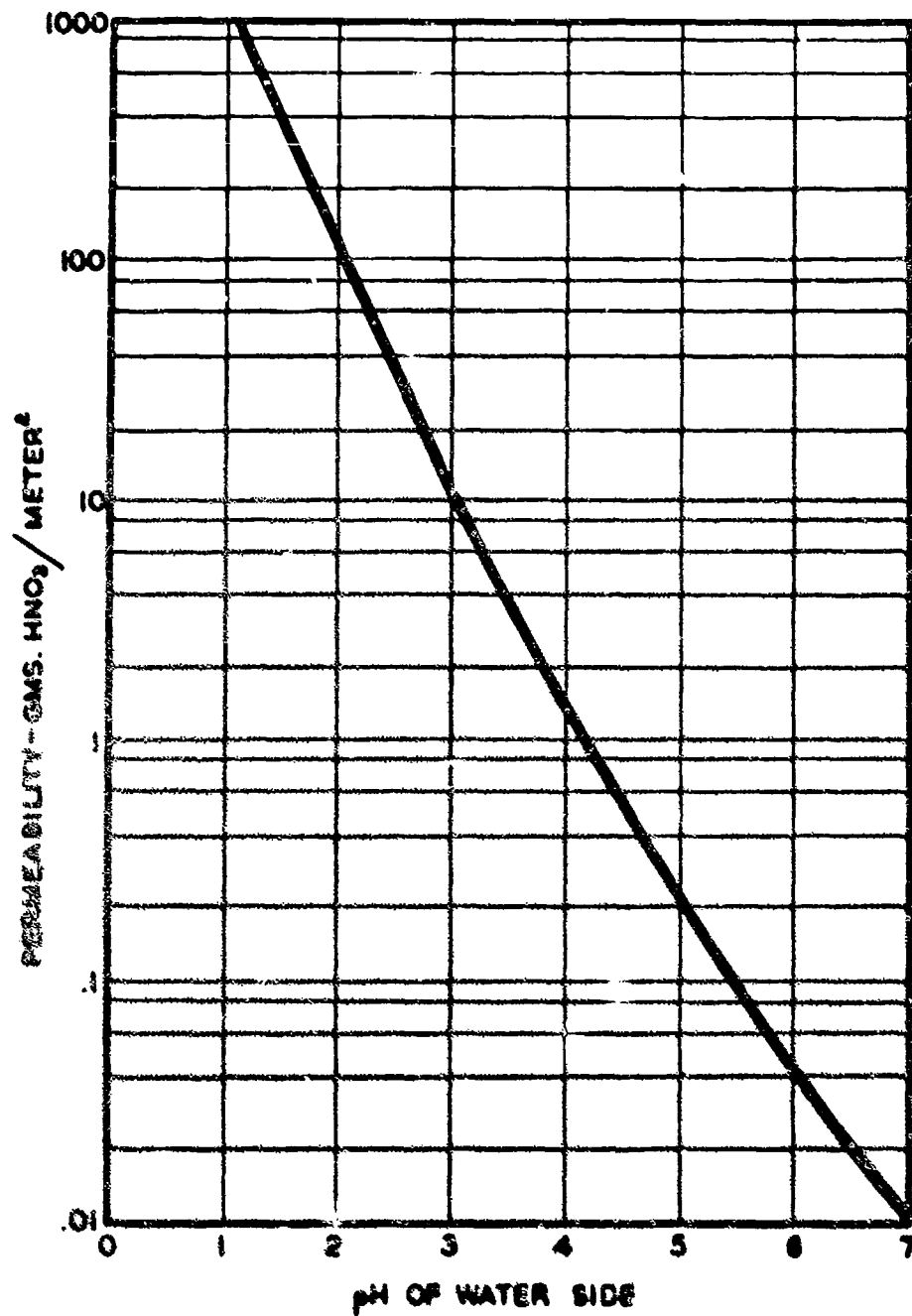


FIG. 24 CALIBRATION CURVE OF TEST CELL

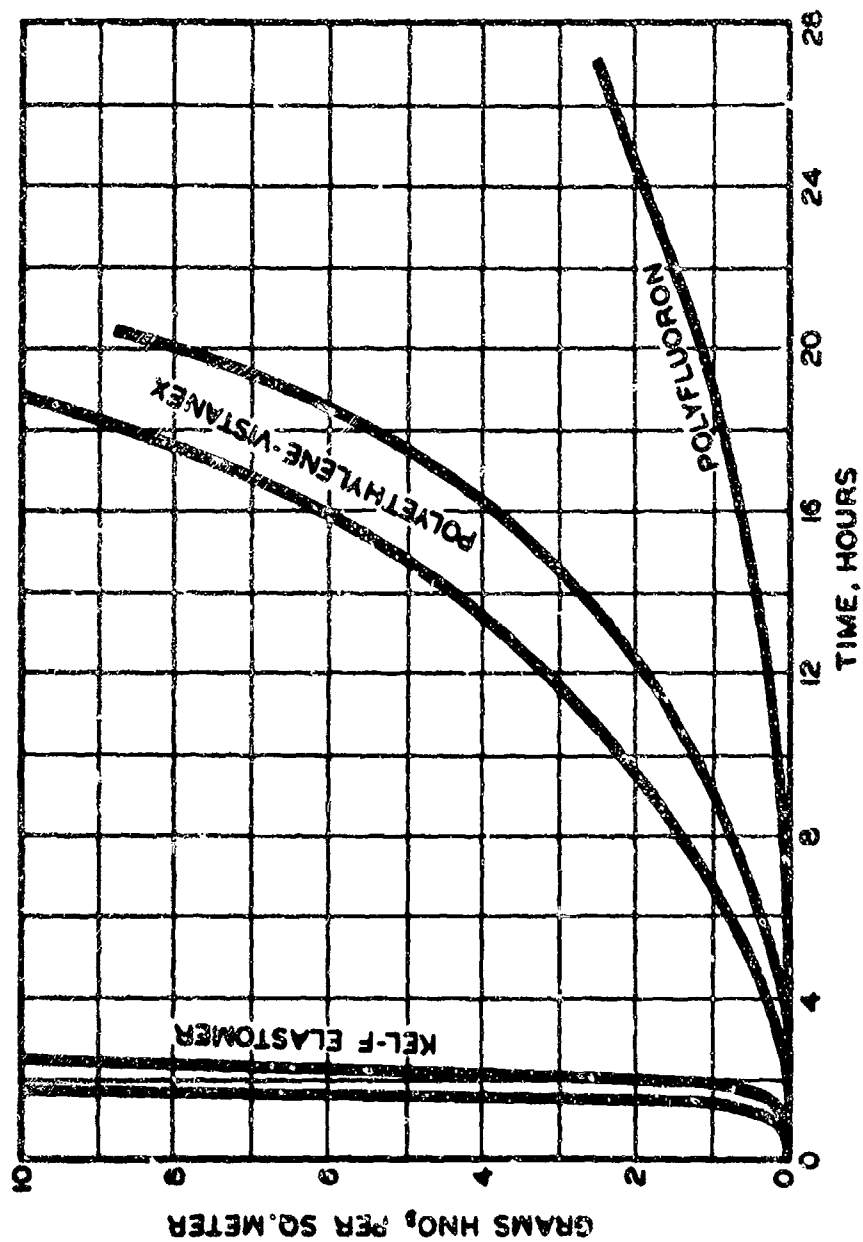


FIG. 25 H-CELL PENETRATION, POLYMER COATINGS  
KNIFE-COATED ON VACAL

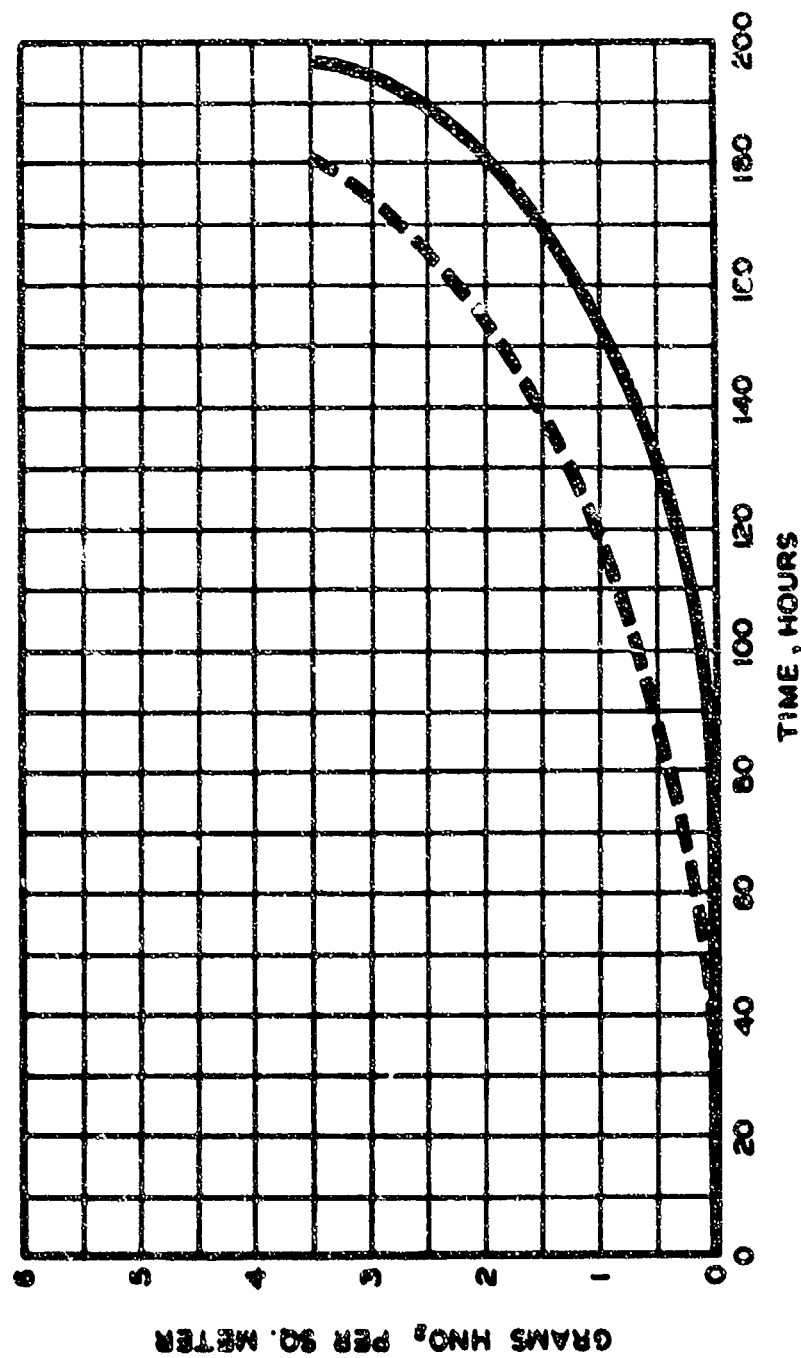


FIG.26 H-CELL PENETRATION, ALUM. PIGMENTED  
POLYFLUORON KNIFE-COATED ON GLASS FABRIC.

Experiment 11: Monoethylaniline-White Fuming Nitric Acid  
Flame Tests

**Object:** To determine the insulation properties of various fabrics when exposed to a brief flame caused by mixing monoethylaniline with white fuming nitric acid, and to determine the properties of such a flame.

**Results:** The flame caused by open mixing of small amounts of white fuming nitric acid and monoethylaniline produced temperatures above 1600°F (indicated by a No. 30 thermocouple wire), but it was of comparatively short duration, with the peak temperature indicated after about 3 seconds. The flame was smoky, and yellow in color. Fabrics placed in such a way that one face was exposed directly to the flame indicated temperatures on the opposite side of the fabrics ranging from 150°F to 380°F.

The results obtained on the different fabrics can be used only for approximate comparisons as there were apparent variations in intensity and effect of the flames in the different tests (see Discussion at the end of this Experiment). It was also apparent, however, that the flames showed a heating effect quite similar to that of the Global Radiant Heat Test (Experiment 3). Most of the heat absorbed by the test fabric in the flame and steam tests was received by conduction from the hot reaction-product vapor rather than by radiation.

The thicker sponge samples showed the best results since they slowed down the conduction. The thin Rayfoil with a highly reflective surface, absorbed and transmitted heat rapidly. Vacuum-deposited aluminum surfaces were apparently no better than aluminum-pigmented polymer surfaces. These data highlight the importance of the sponge and minimize the importance of the radiation coating.

**Materials:** Fabric samples No. 174B, 175, 176 and 177 were described under Experiment 8. The remainder are described below:

- 203. Same as #162, except a coating of clear Polyfluoron (0.002 inch) on the aluminum face.
- 204. Same as #174B (and #174A), except overall thickness 0.075 inch.
- 205. Same as #177, except overall thickness 0.070 inch.

206. Same as #166, except a coating of aluminum-pigmented polyethylene-Vistanex blend (80:20) (0.002 inch) on the fabric face, and overall thickness 0.070 inch.

207. Same as #206, except overall thickness 0.038 inch.

**Procedure:** Two aluminum containers were connected by hinges so that by pulling a wire the contents of the upper container could be thrown quickly into the lower container. A Transite board shield with a 6 x 8 inch rectangular hole in the center was placed beside these containers. The fabric sample was attached across the 6 x 8 opening of a box of inside dimensions 6 x 8 x 6 inches (the same used in the Globar test, Experiment 8), with five thermocouples, inside the box, touching the fabric surface (back). The box was attached to the back of the Transite shield so that the reflective fabric face was exposed, through the 6 x 8 inch hole, to the flame (see Figure 27). A No. 30 iron-constantan thermocouple was placed on the flame side of the Transite shield, about one-quarter inch in front of the fabric sample.

White fuming nitric acid (600 cc) was placed in the lower container and monoethylaniline (200 cc) was placed in the upper container. These were mixed by throwing the small upper container partly over the lower container. Peak temperatures on the front and on the back of the fabric sample, and the times required to indicate the peak temperatures, were recorded.

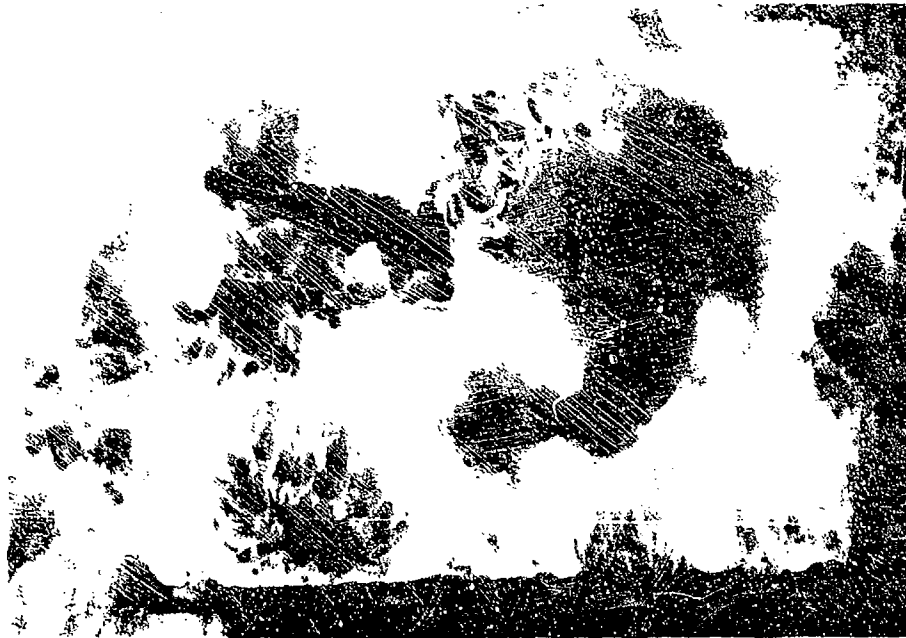
**Data:** See Table 9. All of the samples tested had acid-resistant coatings on the face. None of the samples appeared seriously harmed, although they were covered with the reaction mixture and streaked with carbon. None burned.

**Discussion:** The two sets of data in Table 9 were obtained from tests run on different days, and wind conditions caused considerable difference in the heating effect on the fabrics.

TABLE 9

WHITE FUMING NITRIC ACID-MONOETHYLANILINE FLAME TESTS

Sample No.	Description	Max. Temp. Front		Max. Temp. Back	
		Temp., °F	Time, Sec.	Temp., °F	Time, Sec.
174B	P.F.-Vacal-Sponge (.058")	1400	3	148	60
175	Kel-F.E.-Vacal-Sponge (.045")	1600	3	190	30
177	Al. pig. P.F.-Glass-Sponge (.040")	1350	4	168	50
203	P.C.F.-Rayfoil (.010")	1400	3	380	32
204	P.C.F.-Vacal-Sponge (.075")	1650	3	225	27
205	Al. pig. P.C.F.-Glass-Sponge (.070")	1350	2	198	25
206	Al. pig. P.E.-Vist.-Glass-Sponge (.070")	1650	3	177	25
207	Al. pig. P.E.-Vist.-Glass-Sponge (.038")	1300	4	310	23



2. BURNING TEST



1. BURNING TEST

FIG. 27 PHOTOGRAPH OF FLAME TEST

The problem of protective clothing which exists in connection with rocket propulsion work has been discussed briefly earlier in this report.

In any operation with hazardous chemicals, with even the best equipment design and operation, there may be leakage or the necessity for open handling of dangerous materials. In experimental work with rockets and guided missiles, it is expected that a certain amount of splashing of materials such as white fuming nitric acid will occur. The protective clothing in present use, utilizing a vinyl chloride acid-resistant coating, provides at best minimum protection against such chemical splashing. Under a previous contract, AF 33(616)-155, The Connecticut Hard Rubber Company developed a chemically resistant, coated fabric with a polyethylene-Vistanex coating which provides far greater protection against splashing of oxidants such as white fuming nitric acid (1).

Another serious hazard has been recognized, however, in the leakage of oxidants and fumes during the charging of a missile. This hazard is one of an accidental mixture of spilled oxidant with spilled fuel such as monoethylaniline or hydrazine. Such a mixture would cause an immediate combustion, spattering the reacting materials and products and exposing nearby personnel to flame and temperatures of the order of 1000°F. Against such heat, the vinyl chloride or the polyethylene-Vistanex fabric would provide virtually no protection. The object of this contract was to produce a fabric which would provide personnel with temporary protection in the event of such an accident.

In any consideration of protective clothing, two points are believed to be essential; 1) the garment must afford adequate protection against the hazard involved, and 2) it must not interfere with the worker's movements, thus inducing a secondary hazard (2). In the combustion of corrosive and poisonous materials, one must provide respiratory protection, flame protection for the entire body, and splash protection for the entire body. Such a condition would indicate a complete suit of impervious fabric, acid-resistant and insulated for brief exposure to 1000°F, and fitted for respiration and ventilation. The supply of air to the suit for ventilation would not only provide the required cooling, but would also provide a positive pressure in the suit to minimize the possibility of corrosive materials entering the suit in the

event of an explosion. Although this describes an ideal suit, it is probable that compromises will be made in some of these features for the sake of comfort and working efficiency for the wearer.

Respiratory protection here would require a complete air-supply suit. The air supplied in this case would serve three purposes -- breathing, ventilation, and a small positive pressure inside the suit to minimize the possibility of entry of toxic vapors. It would appear that the air in this case should be supplied by a minimum one-inch-diameter hose of a maximum 150-foot length, connected to a hand- or motor-driven blower located a sufficient distance from the danger area (3). The supply hoses would also have to be protected with a flame- and acid-resistant covering.

The hood of the protective suit should be supplied with a shatterproof heat-resistant glass window, probably of Pyrex. The glass window could be backed by a plastic window, if necessary, with an air space between the two. Also, if it is felt necessary, a light deposit of aluminum could be placed on the outer surface of the glass window, which would serve to reflect heat in the event of ignition. The aluminum coating would reduce the transmission of visible light and therefore may be undesirable.

The remaining two features, those of heat- and flame-protection and chemical-splash protection, were the subject of the present contract and have been investigated extensively.

For heat- and flame-protection, the general types of materials to be considered are: 1) asbestos fabrics, 2) glass fabrics, 3) rock wool fibers and fabrics, and 4) rubbers and plastics. The fifth heat- and flame-resistant material, chrome-tanned leather, will not be considered further, since it is not believed to be adaptable to acid protection or general production techniques required here.

Asbestos fabrics are generally supplied in herringbone weave or basket weave with an asbestos content ranging from 95 percent down. The fabrics generally have five percent or more of cotton mixed in the roving. For flame- and heat-resistant clothing, an asbestos cloth should contain a maximum of sixteen to eighteen percent of cotton, with the remainder asbestos or asbestos and glass (4), (5). The resistance of the asbestos fabrics to radiant heat may be greatly improved by the addition of a coating of aluminum to one side of the fabric. This aluminum coating may be conveniently added by vacuum deposition, foil lamination, or by the use of a highly reflective heat-resistant paint. Samples of

vacuum-aluminized asbestos showing outstanding flexibility and reflectivity have been supplied by the Minnesota Mining & Manufacturing Company. Various articles of clothing fabricated from asbestos fabrics or aluminized asbestos fabrics are available. These include gloves, aprons, coats, boots, leggings, hoods, coveralls and complete suits. A number of such items, including a thick insulated fire rescue suit utilizing the Minnesota Mining & Manufacturing Company aluminum-coated asbestos fabric, are offered by the Industrial Safety Specialties Company, Perkasie, Pennsylvania.

Glass fabrics are available in a wide variety of constructions and weights. These fabrics are strong, relatively heat-resistant, and offer the further advantage of a high degree of chemical resistance. While the heat-resistance of unprotected glass fabric is considerably less than that of asbestos fabric, the addition of an aluminum coating to the glass fabric has been found to increase greatly the heat- and flame-resistance, especially for short-term exposures.

The use of rock wool fibers in clothing is generally limited to thick insulated suit constructions where the fiber batting is contained inside fabric walls. A Thermo-flex heat-resistant blanket construction is offered by Johns-Manville. This consists normally of a refractory fiber filler contained in a stainless steel mesh. Such a construction would be porous and relatively stiff and heavy for clothing use. Several nonwoven ceramic or mineral fabrics are also available. These materials, in general, have lower strength than woven fabrics and are less flexible. They are generally used as insulation or as filter materials.

The best rubbers and plastics have considerably lower heat-resistance than the materials described above, with maximum usable temperatures on the order of 550°-600°F. The silicone rubbers are well known for their high-temperature resistance and are useful up to 550°F, and somewhat higher for short-term exposure. The fluoro-elastomers are in an early stage of development and show considerable promise of heat-resistance. Kel-F Elastomer is presently useful to about 450°F and will withstand exposure to considerably higher temperatures for short periods of time (6). The fluoroplastics such as polytetrafluoroethylene (Teflon) and polymonochlorotrifluoroethylene (Kel-F, Fluorothene, Polyfluoron) are considered heat-resistant as well as chemically resistant (7), (8), (9), (10). Teflon is resistant to temperatures as high as 600°F, while the maximum temperature for Kel-F is somewhat under 400°F. A

material which has shown a fair degree of heat-resistance and chemical-resistance is the Hercules polymer, RD-115 (11). This material, however, is useful only to temperatures somewhat above 350°F. Of the rubbers and plastics mentioned here, only the fluoroplastics of the Teflon and Kel-F type are considered nonflammable. Each of the others can be made flame-resistant and self-extinguishing.

The subject of chemical-splash protection has been reviewed in some detail under a previous contract (AF 33(616)-155). The result of this contract was the development of a fabric coated with a polyethylene-Vistanex blend. A blend of 60 parts Vistanex B-80 and 40 parts polyethylene showed excellent resistance to white fuming acid, as well as desirable flexibility and adaptability to standard fabrication techniques.

Butyl rubber, by virtue of its low unsaturation, showed better resistance to white fuming nitric acid than any of the other hydrocarbon rubbers. Its resistance, compared with that of the polyethylene-Vistanex blend or Kel-F, was, however, relatively poor. The commercially available fluoroplastics, polymonochlorotrifluoroethylene and polytetrafluoroethylene, showed excellent resistance to attack of white fuming nitric acid and other oxidants. Polytetrafluoroethylene, however, does not fuse in fabrication in the same way as other thermoplastic materials, and, as a result, thin films of this material are somewhat porous. The monochlorotrifluoroethylene polymers such as Kel-F and Fluorothene fuse readily to form highly impervious films. In previous work in this laboratory, difficulty has been encountered in producing a satisfactory, flexible and impermeable coated fabric with the Kel-F-type polymers. A new processing technique has become available, however, which has changed this situation.

Exon 400 XR-61 (formerly Veloform P-10) (12), a copolymer of a fluorocarbon monomer and vinyl chloride, showed moderate resistance to white fuming nitric acid. Its resistance to acid-penetration, however, was about one-fourth that of the polyethylene-Vistanex blend (1). Two more commercially available polymers have what is considered good chemical-resistance. These polymers are polyvinylidene chloride and polyvinyl chloride. Hercules RD-115, mentioned above, is somewhat better. The resistance of each of these materials to white fuming nitric acid, however, is rather poor (1), (11).

One of the target requirements for the fabric developed under the present contract was that it should not give off fumes upon application of 1000°F heat, which would injure personnel. This requirement was of particular interest in considering a material such as Kel-F or Teflon as an acid-

resistant barrier on the fabric. A quick review was made of the toxicity of the various materials involved here. For the present purpose, it can be assumed that nitric acid in an open reaction with a material such as monoethylaniline or hydrazine will be reduced to nitric oxide, with the formation of nitrogen dioxide from possible thermal decomposition of nitric acid or from oxidation of the nitric oxide. Thus it would be reasonable to assume that the reaction mixture would contain superheated vapors of nitric acid, nitrogen dioxide, nitric oxide, some water, hydrazine or monoethylaniline, and their reaction products. The most troublesome portion of the fabric with respect to the possible evolution of toxic fumes upon application of 1000°F heat would be the acid-resistant coating on the exposed side of the fabric. All of the materials listed above as potential chemically resistant coating materials, with the possible exception of polyethylene-Vistanex and butyl rubber, could give rise to toxic decomposition products under such temperature conditions. Polyvinylidene chloride and polyvinyl chloride would evolve hydrogen chloride gas. Exon 400 XR-61 would evolve hydrogen chloride gas and possible fluorocarbon decomposition products. The fluoroplastics evolve decomposition products which are known to be toxic (13).

Approximate toxicities of these materials are as follows (14):

Nitric acid, allowable concentration in air 10 ppm or less, 100-150 ppm for 30 minutes is dangerous, 200-700 ppm briefly is lethal (5 to 8 hours later); the symptoms are delayed 5 to 48 hours.

Nitric oxide, allowable concentration in air 25 ppm, toxicity similar but somewhat less than that of nitric acid.

Nitrogen dioxide, allowable concentration in air 10-25 ppm, toxicity similar to that of nitric acid, somewhat less.

Aniline, allowable concentration in air 5 ppm, maximum tolerated for 1 hour, 100-150 ppm.

Monomethylaniline, twice as toxic as aniline.

Ethylaniline, toxicity similar to that of aniline.

Monoethylaniline, no data readily available.

Hydrazine, allowable concentration in air 6 ppm, highly toxic (15).

Hydrogen chloride, allowable concentration in air 5-10 ppm, 1500-2000 ppm lethal in a few minutes, maximum tolerated for 1 hour 50 to 100 ppm.

Decomposition products of polymonochlorotrifluoroethylene and polytetrafluoroethylene, allowable concentration in air somewhat greater than 10 ppm; toxic (13).

Hydrogen fluoride, allowable concentration in air 3 ppm, 50 ppm fatal in 30 to 60 minutes.

All of the materials listed above would be considered highly toxic, with the possible exception of hydrogen chloride. It would seem that such a mixture of toxic materials would require impervious clothing and complete respiratory protection. It would also seem that the addition of a material such as Kel-F or vinyl chloride as an external coating on a fabric with an impervious lining would cause little harm in the existing corrosive and toxic atmosphere.

A brief investigation was made of test methods suitable for evaluation of various fabrics to meet the target requirements of this contract. A Gobar radiant heat test was set up in accordance with Specification MIL-C-8240. Two thermocouples were placed on either side of the fabric to be tested so that the temperature of the "hot side" and the "cold side" of the fabric could be read concurrently. The apparatus was modified by the addition of a shutter or gate, so that when the Gobar was raised to the proper temperature, the shutter could be opened and the fabric exposed for a short, definite period of time.

An excellent method for testing the permeability of various materials to white fuming nitric acid was described as the H-Cell Test in reports covering previous contract work in this laboratory (1), (16). This method is believed to be considerably superior to methods where the passage of the acid is shown merely by the changing of an acid- or oxidation-indicator. In the H-Cell Test, the passage of nitric acid can be measured quantitatively and continuously by measuring the pH of water in contact with the fabric on the side opposite the acid.

In connection with the 1000°F steam test and the white fuming nitric acid-monoethylaniline fire test, described in the Experimental Section of this report, some investigation was made of high-temperature-measurement techniques. An excellent description of the factors involved in high-temperature measurements may be found in a book prepared by the American Institute of Physics (17). In a more recent collection of papers on combustion flame and explosion phenomena, Plock, et al, discussed at some length the radiation errors and conduction errors involved in the use of thermocouples to measure the temperature of jet exhaust gases (18). At 1000°F, it would appear that these errors would be on the order of 30 degrees, or less. In the work for this contract, a correction value could be added for radiation error and conduction error, where applicable, and the resultant temperature value should be well within the practical limits required. A far more serious problem was that of obtaining a sufficiently

rapid indication of temperature in a flame of very short duration. A series of very fine wire thermocouples were connected together to make a type of thermopile as a means of improving the response.

## DISCUSSION

The general problems and the main lines of development involved in this project have been covered in the Introduction and in the Literature and Industrial Survey Sections. The experimental work will be discussed briefly here.

Sponge fabric samples prepared in the initial work on this contract indicated the value of such a construction as a high temperature insulating material and clearly justified the development of a silicone rubber sponge compound specifically for this fabric use. A group of silicone rubber stocks were compared (Experiment 1) and one was selected on the bases of maintaining softness and flexibility as long as possible at high temperature. This stock was further compounded (Experiment 2) to yield a low density sponge suitable for continuous blowing and curing on glass fabric in production equipment. In this study, five different blowing agents and three different curing catalysts, covering a wide range of activating temperatures, were tested over wide variations in concentration. These combinations were blown at temperatures ranging from 300° to 480°F. The results of the study were quite consistent and showed excellent correlation. A reproducible relationship was found between the initial thickness of the rubber-fabric combination and the final blown and cured thickness, specific gravity, and weight of the sponge fabric.

Using the compound developed in Experiment 2, sponge fabric was produced in continuous length on a pilot-scale tower, as described in Experiment 3. The product was of uniform low density and had properties which agreed quite well with those indicated in Experiment 2.

It is sometimes desirable to apply a silicone rubber coating to a fabric in the form of a solvent dispersion. Samples were prepared (Experiment 4) to determine the effect of various amounts of solvent on the blowing efficiency of the silicone rubber sponge compound. As little as 12 percent of solvent added to the sponge compound resulted in a sponge product of considerably higher specific gravity than that obtained without solvent. Toluene was found to be somewhat more harmful to the sponge compound than carbon tetrachloride. Apparently the solvents caused premature decomposition of the sponging agent, and possibly the curing catalyst, in the silicone rubber compound.

It was evident early in the work on this contract that a coating would have to be applied to the reflective surface, or other fabric surface, to protect it in daily use from

accidental splashing with fuming nitric acid and other materials. When a drop of fuming nitric acid was applied to the surface of vacuum deposited aluminum, the aluminum was immediately destroyed. This protective coating should be transparent to radiant heat and at the same time be flexible so that the fabric would not become rigid or stiff. As far as penetration in an actual ignition is concerned, a combination of fabric and thick silicone sponge would apparently be sufficient for brief exposure to the superheated vapors, but it would not be practical to allow the insulating material to be unprotected from accidental splashing in daily use. Experiment 5 was conducted to determine the best methods of applying the various clear acid-resistant materials on the reflective aluminum surface, and for applying the aluminum-pigmented acid-resistant materials on a glass fabric surface. The Polyfluoron (polychlorotrifluoroethylene) and the Kel-F Elastomer were applied readily by standard knife-coating techniques, or by spraying. The polyethylene-Vistenex blend could be applied smoothly by knife-coating, provided the temperature of the coating mixture was properly controlled. This blend could not be spray-coated in the standard spray equipment.

In early attempts to apply a Polyfluoron coating on the Vacal fabric (vacuum deposited aluminum on glass fabric), decomposition of the thin layer of cement between the aluminum and the glass fabric caused a yellow or brown coloration of the clear Polyfluoron coating. However, blowing and curing of the silicone rubber sponge on the back of the Vacal fabric satisfactorily removed this problem, as a Polyfluoron coating subsequently applied to the aluminum surface was not noticeably colored.

No difficulty was found in obtaining satisfactory adhesion of both the Polyfluoron coating and the silicone sponge to the Vacal fabric. On the plain glass fabric, however, penetration of the fabric by either the silicone rubber or the Polyfluoron presented a non-adhesive surface to the material which was applied second. Experiments designed to obtain maximum adhesion of both coatings to the glass fabric are described in Experiment 6. It was found that an initial thin spray-coating of Polyfluoron adhered well to one side of the glass fabric and served as a primer for later Polyfluoron coatings, without filling the interstices of the fabric. The rubber coating adhered well to the opposite, clean side of the glass fabric. Further knife-coatings of Polyfluoron adhered to the primed fabric surface and produced a non-porous coating.

Under a previous contract, AF 33(616)-155, The Connecticut

Hard Rubber Company developed a chemically resistant, coated fabric with a coating of a polyethylene-Vistanex blend (1). In later work dicumyl peroxide was found to produce an appreciable curing effect in the polyethylene and in the polyethylene-Vistanex blends. This curing action was investigated further in connection with the possible use of the polymer blend as an acid-resistant coating material. The effect of the dicumyl peroxide cure on the physical properties of polyethylene and polyethylene-Vistanex blends was shown in Experiment 7. The remarkable resistance to flow exhibited by the cured polyethylene and blends at 250°F was also apparent for shorter periods of time at much higher temperatures (400-600°F). It should be pointed out that at higher temperatures air oxidation occurs at a much greater rate, resulting in a shorter useful life. It is apparent, however, that for short exposures relatively high temperatures may be withstood without appreciable softening or flowing of a cured polyethylene or polyethylene-Vistanex coating.

The resistance of the cured polyethylene and polyethylene-Vistanex blends to penetration by white fuming nitric acid was determined in H-Cell tests. It was quite interesting that the peroxide cure improved considerably the resistance of the polymers to penetration by fuming acid. It was also shown that the resistance of the polyethylene-Vistanex blends was considerably better than that of the polyethylene alone, which agrees with the results found in work under the earlier contract (1).

The application of the peroxide cure to Vistanex blends with the new high-density polyethylene polymers should be of special interest in the preparation of acid-resistant fabrics at ordinary temperatures. The combination of better acid-resistance and resistance to flow at high temperatures would improve further the material developed under the earlier contract.

As indicated in the Introduction to this report, the fabric product developed under this contract was to be resistant to brief exposure to a chemical fire at temperatures up to 1000°F, as well as resistant to white fuming nitric acid and to various fuels. Four tests were devised as a means of comparing samples of the various commercial and experimental fabrics. These tests were (1) radiant heat (Globar) at 1000°F, (2) superheated steam at 1000°F, (3) H-Cell permeability to white fuming nitric acid, and (4) exposure to white fuming nitric acid-monoethylaniline flame. These four tests and the results obtained from the tests are described in Experiments 8 to 11.

As would be expected, the value of a fabric as protection against radiant heat was strongly dependent upon the type of surface presented to the heat source (Experiment 8). A highly reflective aluminum surface allowed comparatively little absorption of the radiant heat. An aluminum foil surface appeared to reflect the heat slightly better than a vacuum-deposited aluminum surface. (The vacuum-deposited aluminum, however, resulted in a much more flexible and pliable fabric.)

Outstanding protection against radiant heat was shown by samples of glass fabric with a vacuum-deposited aluminum coating on the face and a layer of silicone rubber sponge, 0.100 inch or greater in thickness, on the back. These samples showed only a 25 degree rise in temperature on the side opposite to that exposed to 1000°F radiant heat for ten seconds.

It would be expected that a coating of almost any non-metallic material on the face of the aluminum would absorb a considerable amount of heat and thus reduce the efficiency of the aluminum reflective surface. The application of a thin (0.002 inch) polymeric acid-resistant coating on the face of the reflective aluminum surface did not reduce the efficiency of the reflective surface seriously, although the reduction was quite noticeable. Aluminum-pigmented polymeric coatings absorbed more heat than the polymer-coated aluminum surfaces, but were still more reflective than uncoated glass fabric surfaces. The low reflection of the almost white glass fabric surface as compared with that of the aluminum surface could be expected with radiant heat from a relatively low-temperature source. For a body at 1000°F, the wave length of the radiated heat shows a peak at about 3.5 microns (19). Aluminum shows a reflectivity of about 80% to visible light, which increased to 98% at 3 to 4 microns. Most white surface materials (the various oxides, enamels, white fabrics) show relatively high reflectivity for visible light (80 to 98% at 0.6 microns) but this falls off rapidly with increasing wave lengths to values of 10 to 30% at 3 to 4 microns (20).

As indicated in the Introduction to this report, an accidental ignition of fuel and oxidizer would probably produce not only radiant heat in the range of 1000°F, or higher, but would scatter a heated mixture of reactants which at the temperatures involved could be present in the form of highly superheated vapors. The opinion has been expressed that although radiant heat can be readily reflected by a lightweight fabric of the proper construction, a more serious problem is presented by the presence of the superheated vapors. Such a serious problem is well

known to users of present porous asbestos fire-fighting equipment.

In order to conduct a realistic test with such superheated vapors, an apparatus was constructed to generate low-pressure 1000°F steam, to expose the fabric samples to the 1000°F steam for short definite periods of time, and to measure the penetration of vapors through the fabric samples. This apparatus is described in Experiment 9.

To protect against exposure to 1000°F steam, a fabric must have two properties, (1) low thermal conductivity, and (2) no appreciable porosity to the steam. The silicone rubber sponge-fabric provided a high-temperature-resistant, flexible low-density insulating material, and it was found that a relatively thin layer of the silicone rubber sponge (0.020 inch or greater) was sufficient to prevent noticeable penetration of the superheated vapors. A sample of aluminum foil on glass fabric (Rayfoil) allowed no measurable transmission of vapor, but transmitted heat rapidly by conduction.

As would be expected, the presence of a highly reflective surface was of less importance than the thickness of the insulating material, but the effect of the reflective surface was quite noticeable.

The outstanding samples of those tested against 1000°F steam were the thick sponge-fabrics (0.10 and 0.26 inch, weighing only 1.5 and 3.1 pounds per square yard, respectively) which showed maximum temperature rises on the back of only 65 degrees and 50 degrees after a ten second exposure to the 1000°F steam. A heat-reflective surface, while not necessary, was helpful. The various polymeric acid-resistant coatings showed little effect on the results of the steam test.

Methods of application of the various acid-resistant polymeric coating materials on glass fabric were described in Experiments 5 and 6, and were discussed above. Samples of these coatings on glass fabric were tested for resistance to white fuming nitric acid by means of the H-Cell permeability test. In this test, mentioned in the Literature and Industrial Survey and described in Experiment 10, the coated fabric sample was placed as a diaphragm between tubes containing white fuming nitric acid and distilled water. The passage of nitric acid through the diaphragm was indicated quantitatively and continuously by measuring the pH of the water in contact with the fabric on the side opposite the acid. This test quickly showed pin holes or physical flaws in the coating, and also indicated whether passage of the acid through the coating was by physical diffusion alone, or as a

result of chemical attack by the acid on the coating.

In Experiment 10, the H-Cell acid-penetration resistances of the coated-fabric samples were compared. It is felt that the order of the results shown in Figure 25, i.e., Polyfluoron, polyethylene-Vistanex, and Kel-F Elastomer, is correct; this order is in agreement with earlier work done in this laboratory. The results with respect to the Kel-F Elastomer coatings, however, are unusually low. It has previously been found that the acid-penetration resistance of the Kel-F Elastomer is on the same order as that of polyethylene-Vistanex, and considerably less than the resistance of a coating of polychlorotrifluoroethylene. In this series of tests, however, thin coatings of Kel-F Elastomer prepared by several different methods showed relatively low resistance to penetration by white fuming nitric acid.

A knife-coating of aluminum-pigmented Polyfluoron on glass fabric followed by a knife-coating of clear Polyfluoron (final coating thickness 0.002 inch) showed outstanding resistance to penetration by white fuming nitric acid, withstanding 165 to 200 hours' exposure in the H-Cell before passage of 2.5 grams of acid per square meter of exposed area.

A brief test was also run to determine the resistance of the coating materials to monoethylaniline. After 24 hours' immersion in monoethylaniline at room temperature, Polyfluoron showed less than 0.1 percent gain in weight. Polyethylene gained 2.6 percent and cured polyethylene (4 percent peroxide) gained 4.1 percent in weight. A polyethylene-Vistanex blend (50:40) gained 2.9 percent and the cured polyethylene-Vistanex blend (4 percent peroxide) gained 5.7 percent. Kel-F Elastomer (uncured) gained 1.9 percent, and cured Kel-F Elastomer gained 1.3 percent in weight. These results indicate that any of the coatings considered would have sufficient resistance to monoethylaniline to withstand occasional splashing in daily use.

With respect to chemical resistance, the polychlorotrifluoroethylene is considerably better than any of the other materials tested, and may be applied and used in relatively thin coatings (0.001 to 0.002 inch). A disadvantage of the polychlorotrifluoroethylene is its relatively low degree of flexibility. It is considered to be a relatively rigid plastic material while the other coating materials tested (polyethylene-Vistanex and Kel-F Elastomer) may be considered to be elastomeric. In a very thin coating on the sponge-fabric, however, the polychlorotrifluoroethylene appears to be sufficiently flexible, and resistant to wrinkling.

The final test which was applied to the acid- and heat-resistant fabric samples was that of direct exposure to a flame caused by mixing white fuming nitric acid with monoethylaniline. Open mixing of small quantities of white fuming nitric acid with monoethylaniline did not result in a detonation, but the mixture ignited and burned rapidly to produce a relatively low-temperature, yellow, smoky flame. As would be expected from the nature of the reactants, the open combustion proceeded in two stages. First, there was burst of flame which dissipated quickly, leaving a small low-temperature fire burning on the spattered reactant materials. Even the initial flash appeared to be one of relatively low temperature, from the dark, yellow and black color and from the amount of unburned carbon in the flame and drifting around after the flash. Thermocouples placed in the flame (three feet above the reactant mixture, and directly in front of the exposed fabric) showed a maximum indication of about 1650°F, which was reached in about 3 seconds after mixing. The temperature, indicated by the thermocouples, then dropped rapidly to a value below 300°F within 8 to 10 seconds after mixing the ingredients. In most cases, the remaining flames died out in less than one minute.

Because of the relatively low temperature of the flames and the reaction-vapor content, the flame showed a heating effect on the test fabrics quite similar to that of the 1000°F steam, and different from that of radiant heat from the Globar. It would appear that a protective fabric for use under these conditions should be non-porous to the superheated vapors and should have sufficient thickness (and low thermal conductivity) to prevent appreciable penetration, or conduction, of the heat through the fabric. A highly reflective surface on the protective fabric would be quite helpful at some distance from the heat source, but apparently added little value in direct exposure to the flame and heated-vapor mixture.

As a result of the evaluation tests, an aluminum-pigmented polychlorotrifluoroethylene coating on No. 116 glass fabric and silicone rubber sponge, with an overall thickness of 0.070 inch, was recommended to satisfy the requirements of this contract. An alternate recommendation was the same construction with an aluminum-pigmented polyethylene-Vistanex coating in place of the polychlorotrifluoroethylene. The first-recommended construction showed outstanding resistance to white fuming nitric acid, monoethylaniline, and is resistant to virtually all other oxidizers and fuels. It provided good protection against penetration of heat from actual exposure to a white fuming nitric acid - monoethylaniline flame and to 1000°F steam.

The fabric construction is flexible and useful over a temperature range of  $-80^{\circ}\text{F}$  to  $+390^{\circ}\text{F}$ . The construction provided less protection from  $1000^{\circ}\text{F}$  radiant heat than others with more highly reflective surfaces, but the actual flame hazard concerned was found to produce relatively little radiant heat.

The second (alternate) construction, relatively less expensive, showed good resistance to white fuming nitric acid and monoethylaniline, although not as good as the first construction. The remainder of the construction is the same as the first construction and the insulation value is the same. The polyethylene-Vistanex coating will burn, in contrast to the first coating, but this effected no difference in the actual flame exposure test results.

A practical method is now available for the application of the polychlorotrifluoroethylene as a thin, transparent, flexible and impermeable film on glass fabric. Although this film is less flexible and costs considerably more than the polyethylene-Vistanex, its properties are felt to be far superior for the present application.

A thickness of 0.070 inch for the fabric construction has been recommended to provide the required insulation against a 10 second exposure to  $1000^{\circ}\text{F}$ . The actual flame reaction caused by mixing white fuming nitric acid and monoethylaniline produced considerably higher temperatures (approximately  $1600^{\circ}\text{F}$ ), but of much shorter duration (peak temperature in 2 to 4 seconds, with a rapid decrease to below  $300^{\circ}\text{F}$  in another 5 seconds or less). It is possible that a thinner fabric (0.040 to 0.050 inch) might be sufficient if actual-use conditions prove that the flash flame is of less duration than the 10-second target specification. Thinner constructions would have certain obvious advantages, such as in weight and comfort.

## SUMMARY AND CONCLUSIONS

1. A fabric consisting of a thin coating (0.002 inch) of aluminum-pigmented polychlorotrifluoroethylene on glass fabric backed with a low-density silicone rubber sponge, and with overall thickness of 0.070 inch, is recommended for protection against splashing with white fuming nitric acid, and with various fuels, and against exposure to a brief chemical fire (1000°F for 10 seconds) resulting from accidental mixture of white fuming nitric acid and monoethylaniline, or mixture of other oxidizing agents and fuels.
2. An alternate recommendation is the same construction with an aluminum-pigmented polyethylene-Vistanex coating in place of the polychlorotrifluoroethylene.
3. A fabric consisting of an aluminum reflective surface reinforced with glass fabric and backed with a relatively thin layer of silicone sponge rubber was satisfactory as a heat-resistant insulating fabric for short exposure to radiant heat at 1000°F and to superheated steam at 1000°F. It was also impervious to superheated steam at 1000°F for a short exposure.
4. A low-density, silicone rubber sponge compound which can be continuously blown and cured on glass fabric in standard production equipment was developed.
5. A coating of polychlorotrifluoroethylene 0.002 inch in thickness on glass fabric withstood 165-200 hours<sup>1</sup> exposure to white fuming nitric acid before penetration of 2.5 grams of acid per square meter of exposed surface. Polyethylene-Vistanex and Kel-F Elastomer showed considerably lower resistance to penetration by the acid.
6. Polyethylene and polyethylene-Vistanex blends were cured by peroxide to render greatly improved dimensional stability at temperatures of 250°F, and higher. The peroxide cure also effected improved resistance to penetration by white fuming nitric acid.

# BIBLIOGRAPHY

1. Homeyer, H. N., and Becker, J. Coated Fabric for Use in Protective Clothing. WADC Technical Report 54-93, March, 1954.
2. Blake, H. P. Industrial Safety. Second Edition, Prentice-Hall, Inc., New York, 1953. p. 385.
3. Accident Prevention Manual for Industrial Operations. National Safety Council, Chicago, 1946. p. 426.
4. Ibid. p. 437.
5. Military Specification MIL-C-824C and Amend. 1 (USAF). Cloth, Asbestos, Glass, Cotton, Aluminized.
6. M. W. Kellogg Company. Kel-F Elastomer, A First Report on a New Fluorocarbon Rubber. March 15, 1954.
7. E. I. duPont de Nemours & Company, Inc. Information Bulletin A-6251. Teflon.
8. M. W. Kellogg Company. Technical Bulletin #1-3-53. Kel-F.
9. Bakelite Company. Fluorothene Resins, Technical Data (1954).
10. Acme Resin Corporation. Polyfluoron Bulletin (1954).
11. Hercules Powder Company. Polymer RD-115. June 1953.
12. Firestone Plastics Company. Epon 400 XR-61 Technical Bulletin.
13. Hagemeyer, D. R., and Stubblebine, W. Physiological Activity of Fluorocarbon Polymers. Modern Plastics. Volume 31. August 1954. p. 136.
14. Sax, N. I. Handbook of Dangerous Materials. Reinhold Publishing Corporation, New York, 1951.
15. Krop, S. Toxicity and Health Hazards of Rocket Propellants. Paper No. 124-54, delivered before a meeting of the American Rocket Society, January 1954.
16. Kidwell, A. S., et. al. Development of Resilient Materials for Low Temperature Service in the Presence of Aviation Fuels and Lubricants. Report No. 4, June 1952, Contract W0as 51-7666. Bureau of Aeronautics, United States Navy.

17. American Institute of Physics. Temperature, Its Measurement and Control in Science and Industry. Reinhold Publishing Corporation, New York, 1941.
18. Flock, E. P., Olsen, L. O., and Freeze, P. D. "The Use of Thermocouples in Streaming Exhaust Gas." Third Symposium on Combustion Flame and Explosion Phenomena. Williams and Wilkins Company, Baltimore, 1949.
19. Herrington, L. P. Theory of, and Appropriate Methods for Measurement of Surface Emittance. Special Technical Bulletin No. 119, American Society for Testing Materials, Philadelphia, 1951.
20. Handbook of Chemistry and Physics. Thirty-Third Edition pp. 2451-3.

TABLE 10

DESCRIPTION AND SOURCE OF COMMERCIAL MATERIALS

<u>Material</u>	<u>Description</u>	<u>Source</u>
Globar, Type AT	5/16 inch bar, silicon carbide	The Carborundum Company
Kel-F Elastomer	fluorocarbon elastomer	M. W. Kellogg Company
Polyfluoron	polychlorotrifluoroethylene	Acme Resin Corporation
Dispersant "A"	chlorinated hydrocarbon	Acme Resin Corporation
Rayfoil	0.001 inch aluminum foil on glass fabric	Promet Industries
Vacuum-deposited aluminum coating	Thin coating applied on No. 116 glass fabric	Minnesota Mining & Manufacturing Company
Vistanex B-80	polyisobutylene	Enjay Company, Inc.